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Environmental Impacts of the Use of Orimulsion®

Report to Congress on Phase 1 of the Orimulsion® Technology Assessment Program

Volume 1: Executive Summary, Report, and Appendix A

Foreword

The U.S. Environmental Protection Agency is charged by Congress with protecting the Nation's land, air, and water resources. Under a mandate of national environmental laws, the Agency strives to formulate and implement actions leading to a compatible balance between human activities and the ability of natural systems to support and nurture life. To meet this mandate, EPA's research program is providing data and technical support for solving environmental problems today and building a science knowledge base necessary to manage our ecological resources wisely, understand how pollutants affect our health, and prevent or reduce environmental risks in the future.

The National Risk Management Research Laboratory (NRMRL) is the Agency's center for investigation of technological and management approaches for preventing and reducing risks from pollution that threaten human health and the environment. The focus of the Laboratory's research program is on methods and their cost-effectiveness for prevention and control of pollution to air, land, water, and subsurface resources; protection of water quality in public water systems; remediation of contaminated sites, sediments and ground water; prevention and control of indoor air pollution; and restoration of ecosystems. NRMRL collaborates with both public and private sector partners to foster technologies that reduce the cost of compliance and to anticipate emerging problems. NRMRL's research provides solutions to environmental problems by: developing and promoting technologies that protect and improve the environment; advancing scientific and engineering information to support regulatory and policy decisions; and providing the technical support and information transfer to ensure implementation of environmental regulations and strategies at the national, state, and community levels.

This publication has been produced as part of the Laboratory's strategic long-term research plan. It is published and made available by EPA's Office of Research and Development to assist the user community and to link researchers with their clients.

E. Timothy Oppelt, Director
National Risk Management Research Laboratory

EPA REVIEW NOTICE

Environmental Impacts of the Use of Orimulsion®

Report to Congress on Phase 1 of the Orimulsion® Technology Assessment Program

Volume 1. Executive Summary, Basic Report, and Appendix A

By

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Abstract

Orimulsion, a bitumen-in-water emulsion produced in Venezuela, was evaluated to provide a better understanding of the potential environmental impacts associated with its use as a fuel. A series of pilot-scale tests were conducted at the U.S. Environmental Protection Agency's Environmental Research Center in Research Triangle Park, NC, to provide data on emissions of air pollutants from the combustion of Orimulsion 100 (the original formulation), Orimulsion 400 (a new formulation introduced in 1998), and a No. 6 (residual) fuel oil. These results, and results of full-scale tests reported in the technical literature, were evaluated to determine the potential air pollutant emissions and the ability of commercially available pollution control technologies to adequately reduce those emissions. Emissions of carbon monoxide (CO), oxides of nitrogen (NO_x), sulfur dioxide (SO_2), sulfur trioxide, particulate matter (PM), and organic and metal hazardous air pollutants (HAPs) were measured from each of these three fuels to provide a comparison between the "new" fuel (Orimulsion) and a fuel that has been commonly used in the U.S. (the No. 6 fuel oil). Results indicate that CO, NO_x, and PM emissions are likely to be nearly the same as those from the No. 6 fuel oil, that SO_2 emissions can increase if the fuel sulfur content increases, that the particles generated by Orimulsion 100 and 400 are likely to be smaller in diameter than those generated by No. 6 fuel oil, and that HAPs are also likely to be similar to those from No. 6 fuel oil. Both the full-scale results found in the literature and the pilot-scale results measured at EPA indicate that conventional air pollution control technologies can effectively reduce emissions to very low levels, depending upon the type of technology used and the desired emission levels. Because the bitumen in Orimulsion is heavier than water and due to the presence of a surfactant in the fuel, spills of Orimulsion are likely to be more difficult to contain and recover than are spills of heavy fuel oil, especially in fresh water. Additional study is needed before adequate containment and response approaches can be developed. Little, if any, work has been conducted by the fuel producer or the scientific community to address the remaining spill-related issues.

Preface

This report is the result of a request by the U.S. Congress to receive scientific information regarding the potential environmental impacts of the use of Orimulsion as a fuel. In the second half of the 1990s, there was considerable interest on the part of electric utilities in using Orimulsion, which was promoted as a low-cost fuel that could replace heavy fuel oil or coal. There were also many concerns raised by the environmental community regarding the environmental impact associated with switching to Orimulsion. In 1997, the U.S. Congress requested that the U.S. Environmental Protection Agency (EPA) conduct a study to evaluate the potential environmental impacts associated with the use of Orimulsion. EPA's Office of Research and Development provided funds to the National Risk Management Research Laboratory (NRMRL) to conduct this study, and a team of EPA experts in air pollution control, spill response, health effects, and environmental assessment was assembled to carry out the investigation. This report was prepared by EPA staff using data generated at EPA facilities as well as data collected from the general literature.

In 1998, Bituménes Orinoco (Bitor), the manufacturer of Orimulsion, changed the formulation of the fuel. The original fuel, renamed Orimulsion 100, was replaced with a new formulation named Orimulsion 400. Compared to the amount of information on Orimulsion 100, there is relatively little data on the performance of Orimulsion 400. While this report provides as much data as possible on the emissions and performance of Orimulsion 400, the bulk of the data are for the older formulation (Orimulsion 100). Although Orimulsion 100 is no longer produced, the results presented here are still believed to adequately describe the basic behavior of both formulations of Orimulsion. The key question to be addressed in this study is, "Is Orimulsion significantly different from other fossil fuels, and if so, how?" The differences between Orimulsion 100 and Orimulsion 400, as indicated both from the available data and the information provided by the manufacturer, are substantially smaller than the differences between Orimulsion and other fossil fuels. The report distinguishes between the two formulations where appropriate, but uses the generic term "Orimulsion" where such distinction is either unimportant or misleading. The recent reformulation is significant with respect to the surfactant used (which will affect spill toxicity) and the use of a magnesium-based additive (which will affect boiler tube deposition and particulate matter emissions). Other environmental issues appear to be impacted only to a minor degree by the change in formulation.

The emphasis of this report is on generation and control of air pollutants from the combustion of Orimulsion. Although there are other environmental issues associated with the use of Orimulsion, particularly spills of the fuel into water, EPA and NRMRL were advised on several occasions that questions related to air pollutant generation and control were the key unknowns associated with understanding the environmental impact potential of Orimulsion. The initial step in EPA's research activities was the convening of a workshop to discuss environmental issues related to Orimulsion use. This workshop, held February 8, 1998, concluded that there was a lack of information on particle size distribution and composition and on emissions and control of sulfur trioxide from Orimulsion combustion. The workshop also concluded that enough data existed to allow a comparative risk analysis for heavy fuel oil and Orimulsion, and therefore additional research in that area was not immediately required. The workshop noted that a lack of data existed describing the behavior, fate, and effects of Orimulsion spills in fresh water. However, the workshop concluded that investigations into these areas should be the responsibility of Bitor in the event they sought to market the fuel to users where spills into fresh water were possible. Considerable work has been conducted to quantify behavior, fate, and effects of Orimulsion in saltwater environments under the oversight of the International Orimulsion Working Group, of which Bitor is a member and the major source of funding. Thus this report has as its focus the generation and control of air pollutants, although other topics are also covered.

This focus was emphasized in the Orimulsion Technology Assessment Plan that was prepared to guide EPA's research efforts. This plan was reviewed and approved, with modifying comments, by a

panel of technical experts, mostly from outside the federal government. The only exception was one member from the U.S. Coast Guard. The Plan was then reviewed by the Office of Management and Budget (OMB), the U.S. Department of Energy, and the Office of Science and Technology Policy. EPA responded to comments made by each of these organizations and revised the Plan, which was approved by OMB on April 22, 1999.

The National Risk Management Research Laboratory was the lead organization for the study, and was chiefly responsible for preparation of Chapters 1-5 and 9-12. Robert E. Hall was the overall program lead, and C. Andrew Miller was the lead author of these chapters. Kevin Dreher of the National Health and Environmental Effects Research Laboratory prepared Chapter 6, on toxicity testing, with substantial assistance from Adriana Crain. Chapter 7, on spills, was prepared with assistance from Royal J. Nadeau of EPA's Office of Solid Waste and Emergency Response. Randall Wentsel of the National Center for Environmental Assessment prepared Chapter 8, on environmental assessment.

The conclusions stated in this report are scientific conclusions, and are not intended to provide guidance relative to regulatory requirements that may or may not apply to the use of Orimulsion.

Nomenclature and Acronyms

APCS .... air pollution control system
API .... American Petroleum Institute
APPCD .... Air Pollution Prevention and Control Division
ARD .... Arizona road dust
ASTM .... American Society for Testing and Materials
BALF .... bronchoalveolar fluid
bbl .... barrels, U.S. petroleum
BTEX .... benzene, toluene, ethylene, and xylenes
Btu .... British thermal unit
CAA .... Clean Air Act
CAAAs .... Clean Air Act Amendments of 1990
CARB .... California Air Resources Board
CE .... Combustion Engineering
CEM .... continuous emission monitor
CO .... carbon monoxide
CO_2 .... carbon dioxide
DAS .... data acquisition system
DQI .... data quality indicator
EDX .... energy dispersive x-ray
ENEL .... Italian Electricity Generating Board
EPA .... Environmental Protection Agency
ESP .... electrostatic precipitator
FETC .... U.S. Department of Energy's Federal Energy Technology Center
FGD .... flue gas desulfurization
FPL .... Florida Power & Light Company
GIS .... geographical information systems
HAP .... hazardous air pollutant
HEPA .... high efficiency particulate air
HFO .... heavy fuel oil
HQ .... health quotient
IOWG .... International Orimulsion Working Group
IURE .... inhalation unit risk estimate
LAPIO .... low API oil
LDH .... lactate dehydrogenase
LNB .... low NO_x burner
LOEC .... lowest observable effects concentration
LOEL .... lowest observed effect level
LOI .... loss on ignition
MACS .... miniature acid-condensation system
MDL .... method detection limit
MEI .... maximum exposed individual
MIR .... maximum individual risk
NCEA .... National Center for Environmental Assessment
NHEERL .... National Health and Environmental Effects Research Laboratory
NO .... nitric oxide
NOEC .... no observable effects concentration
NO_x .... nitrogen oxides
NRC .... National Research Council

Nomenclature and Acronyms (Continued)

NRMRL . . . . National Risk Management Research Laboratory
NSPS . . . . New Source Performance Standard
O_2 . . . . oxygen
OERR . . . . Office of Emergency and Remedial Response
OFA . . . . overfire air
ORD . . . . Office of Research and Development
ORI 100 . . . . Orimulsion 100
ORI 400 . . . . Orimulsion 400
OSWER . . . . Office of Solid Waste and Emergency Response
OTAP . . . . Orimulsion Technology Assessment Plan
PAH . . . . polycyclic aromatic hydrocarbon
PBS . . . . Package Boiler Simulator
PC . . . . pulverized coal
PDVSA . . . . Petroléos de Venezuela, S.A.
PEA . . . . performance evaluation audit
PM . . . . particulate matter
$PM_{2.5}$ . . . . particulate matter smaller than 2.5 μm in aerodynamic diameter
PM_{10} . . . . particulate matter smaller than 10 μm in aerodynamic diameter
ppm . . . . parts per million
QA . . . . quality assurance
QAPP . . . . quality assurance project plan
QC . . . . quality control
ROFA 6 . . . . residual oil fly ash (No. 6 fuel oil)
RSD . . . . relative standard deviation
SASS . . . . source assessment sampling system
SCR . . . . selective catalytic reduction
SEM . . . . scanning electron microscope
SMPS . . . . scanning mobility particle sizer
SNCR . . . . selective noncatalytic reduction
SO_2 . . . . sulfur dioxide
SO_3 . . . . sulfur trioxide
SVOC . . . . semivolatile organic compound
TCLP . . . . toxicity characteristic leaching potential
THC . . . . total hydrocarbon
TSA . . . . technical systems audit
VOC . . . . volatile organic compound
VOST . . . . volatile organic sampling train
WLFO . . . . wet limestone forced oxidation
XRF . . . . X-ray fluorescence

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Executive Summary

Conclusions of the Report
- Orimulsion is physically and chemically an emulsified heavy fuel oil with elevated sulfur, vanadium, and nickel content.
- Emissions of air pollutants from Orimulsion are not fundamentally different in character from those from other fossil fuels. Orimulsion will in general emit more pollutants than natural gas, about the same as heavy fuel oil, and less than pulverized coal. These comparisons do not hold for all cases, and are based on emission levels without air pollution control systems.
- Results from both full- and pilot-scale tests indicate that emissions from the combustion of Orimulsion can be adequately controlled using commercially available air pollution control technologies that are properly designed and operated.
- Previous experience with Orimulsion indicates that conversion to the fuel may require significant changes to existing equipment, including air pollution control systems, fuel supply and handing systems, and boiler internal components.
- In general, Orimulsion generated PM emissions that were capable of producing significant adverse acute pulmonary toxicity, very similar to the No. 6 fuel oil tested. In all cases, PM from both Orimulsion formulations and the No. 6 fuel oil showed measures of toxicity greater than or equal to either Arizona road dust or saline solution.
- The behavior of Orimulsion in a spill is significantly different than that of most other fossil fuels.
- A review by an EPA-chosen expert panel of a utility-funded ecological risk assessment of a potential spill in the Tampa Bay, Florida marine environment agreed with the assessment's conclusion that a spill of Orimulsion 100 likely poses a similar or lower risk to Tampa Bay biota than does an equivalent spill volume of No. 6 fuel oil. This review was limited to the scope of the original report, and did not examine other factors that may have significant adverse ecological and health impacts.
- The most likely use of Orimulsion in the U.S. in the short term is as a replacement for heavy fuel oil, due to similarity in handling and combustion properties, the price differential between the two fuels, and the readiness of plants using heavy fuel oil to accept tanker shipments of Orimulsion. These factors would indicate that Orimulsion is most likely to be used along the Atlantic and Gulf coasts in the U.S.
- The major gaps in understanding Orimulsion behavior are in freshwater spill response and effects. Further work in this area should primarily be the responsibility of the fuel's suppliers and users, and should not be considered as part of the Congressional directive to provide improved scientific information on the environmental impacts of Orimulsion use. EPA and the U.S. Coast Guard have requested the National Academy of Sciences to conduct a study on Orimulsion to evaluate what additional information is required to effectively respond to freshwater spills. EPA should continue to evaluate spill effects, behavior and response as appropriate in support of their legislated responsibility for spill prevention, preparedness, and response.

Recommendations of the Report
The following recommendations are made with regard to Orimulsion behavior, its potential environmental impacts, and EPA's role in further studies:

1. Based on the results of Phase I of the Orimulsion Technology Assessment Plan, it is not necessary for EPA to proceed with Phases II and III.
2. From the perspective of air pollutant formation and control, Orimulsion should be considered to be a heavy fuel oil, albeit with some properties that require special attention.
3. Studies of Orimulsion behavior in freshwater spills are needed in the event that Orimulsion is transported along fresh waterways or used in situations where spills can reach fresh water, even indirectly. This research should evaluate the effects and behavior of Orimulsion under different conditions (water density, presence of silt or other solids, energy level of waves) and should evaluate means of containing and responding to spills. Bitor or the end user should be responsible for the cost of any such work that directly supports efforts to market Orimulsion

in the U.S. EPA should continue to follow any work conducted by others on the behavior and fate of Orimulsion spills, and should conduct the research necessary to support their legislated responsibility for spill prevention, preparedness, and response, outside the scope of the Congressional directive to provide improved scientific information on the environmental impacts of Orimulsion use.
   4. Research recommended in a review by an EPA-chosen panel for improvements to a utility-funded ecological risk assessment of a potential spill in the Tampa Bay, Florida marine environment is considered to be the responsibility of Bitor.

Purpose and Approach
The purpose of this report is to address the request by Congress that the U.S. Environmental Protection Agency (EPA) "provide better scientific data on the qualities and characteristics of this product [Orimulsion*] and the potential environmental impact of its introduction" into commerce. To address this request, a team led by EPA's National Risk Management Research Laboratory (NRMRL) conducted research to examine the potential environmental impacts associated with the use of Orimulsion as a fuel and prepared this report. The EPA research team included Office of Research and Development (ORD) staff from NRMRL, the National Health and Environmental Effects Research Laboratory (NHEERL), the National Center for Environmental Assessment (NCEA), and Office of Solid Waste and Emergency Response (OSWER) staff from the Office of Emergency and Remedial Response (OERR).

It is not the objective of this report to address possible regulatory requirements or to estimate the costs associated with meeting such requirements. In each case, there are many site-specific factors that are determined by local regulatory requirements and that can significantly impact the cost of converting to Orimulsion. The data and the conclusions presented in this report should not be considered as endorsing or discouraging the use of Orimulsion. The conclusions of this report cannot be considered as identifying specific approaches for meeting regulatory requirements.

In response to reviews of Orimulsion research needs by an interagency panel and a panel of external technical experts, EPA prepared an Orimulsion Technology Assessment Plan (OTAP) to guide its research efforts. The reviewers identified the generation and control of air pollutant emissions and the toxicity of those emissions as the key areas of needed research. Orimulsion spill response, containment, and recovery, and the ecological effects of such spills (particularly in fresh water) were considered to be less critical, and could be addressed as needed by the appropriate party or parties. The OTAP outlined a phased approach, with the need for subsequent phases to be determined by any significant questions identified during preceding phases. This report describes the efforts, results, and conclusions of Phase I of the OTAP.

The key questions addressed by this report are:

   1. Are the emissions from the combustion of Orimulsion significantly different than those from other fossil fuels, and if so, how?
   2. Can the emissions from the combustion of Orimulsion be adequately controlled using existing air pollution control technologies? If not, are there modifications to existing technologies that can be made to adequately control emissions, or are new control technologies required?
   3. Is the behavior of Orimulsion during a spill significantly different than the behavior of other fossil fuels, and if so, how?
   4. What gaps in understanding the behavior of Orimulsion exist, based on the behavior of other fossil fuels and the known properties of Orimulsion? Are these gaps serious with respect to understanding the potential environmental impacts, and if so, what research should be conducted to address these gaps?

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*Orimulsion is a registered trademark of Bitumenes Orinoco, S.A.

Background
Orimulsion is a liquid fossil fuel consisting of an emulsion of approximately 70% bitumen (a naturally occurring heavy petroleum material) from the Orinoco region of Venezuela, approximately 30% water, and a small amount of surfactant to ensure stability of the emulsion. The fuel consists of small (8-24 μm diameter) droplets of bitumen emulsified in water and the surfactant. Orimulsion is produced by Bitúmenes Orinoco, S.A. (Bitor), a subsidiary of the Venezuelan national oil company Petróleos de Venezuela, S.A. (PDVSA), and derives its name from the combination of "Orinoco" and "emulsion."

In recent years, Orimulsion has been proposed as a fuel to replace either coal or heavy fuel oil in utility power plants throughout the world. Orimulsion is currently being used as the primary fuel at nine power plants in Canada, Denmark, Italy, Japan, and Lithuania, representing 3,866 MW of electric power generating capacity and approximately 7.5 million tons of fuel consumption per year. To date, no plant in the U.S. has used the fuel for other than short-term testing.

Air Emissions
Available technical literature (24 references describing air pollutant emissions at 9 full-scale sites and 3 pilot-scale facilities) was reviewed to determine what problems and issues were believed to be most important with respect to air pollutant emissions and control, and to evaluate the levels of emissions experienced by full-scale systems using Orimulsion. Table ES-1 presents a summary of data reported in the literature for Orimulsion and heavy fuel oil. SO_2 and PM data are for pollutant concentrations upstream of any control device.

The reports indicated that CO emissions could be easily controlled by increasing combustion air levels. In general, the conventional techniques used to reduce NO_x emissions from oil combustion (staged combustion, reburning, selective catalytic reduction) were reported to be applicable to Orimulsion. CO and NO_x were dependent upon boiler O_2 and the combustion system design, similar to other fossil fuels. SO_2 concentrations from Orimulsion [upstream of any flue gas desulfurization (FGD)] were consistent with SO_2 concentrations from other fuels with similar sulfur contents. The literature reported that conventional FGD systems could remove up to 95% of SO_2 generated by the combustion of Orimulsion. This would result in controlled emissions of approximately 125 ppm. Full-scale results demonstrated that electrostatic precipitators (ESPs) can be used to control PM emissions to a level similar to those of other fossil fuels.

Emissions of hazardous air pollutants were similar for both Orimulsion and fuel oil. Due to the elevated levels of metals in Orimulsion, metal emissions were higher than organics, with nickel and vanadium being found in the highest concentrations. Although vanadium is not listed as a hazardous air pollutant under Title III of the Clean Air Act Amendments of 1990, it is of concern because of its potential for causing acute pulmonary damage when inhaled. Nickel concentrations in Orimulsion flue gas were higher than those from heavy fuel oil, but both iron and zinc concentrations were higher in heavy fuel oil flue gases than in those from Orimulsion. Processes have been designed to allow recovery of Ni and V in Orimulsion. At least two plants are currently sending Orimulsion ash to facilities for recovery of one or both metals, thereby reducing solid waste streams.

Data From EPA Pilot-Scale Tests
Two formulations of Orimulsion (one commercially available [Orimulsion 400] and one discontinued [Orimulsion 100]) and a No. 6 fuel oil were individually tested in a pilot-scale combustor located at EPA's Environmental Research Center to allow direct comparison of emissions. Concentrations of CO, NO, SO_2, SO_3, and PM were measured, as were concentrations of volatile and semivolatile organic compounds and metals. Measurements of emissions from the different fuels were compared to determine any differences in the amount or character of emissions. The tests were conducted following NRMRL Quality Assurance Level II procedures, which included audits of measurement equipment and review of data by outside organizations.

Table ES-1. Summary of air pollutant concentrations reported in the literature for Orimulsion and heavy fuel oil (SO_2 and PM values are upstream of any control device).

Pollutant	Literature Orimulsion[1]	Literature Heavy Fuel Oil
CO	30-100 ppm[2] (4 tests)	30-100 ppm (4 tests)
NO_x	80-400 ppm (10 tests)	180-420 ppm (6 tests)
SO_2[3]	2500 ppm	1200 ppm[4]
SO_3[5]	2-15 ppm (6 tests)	4-12 ppm (2 tests)
PM[3]	160-350 mg/Nm^3 (8 tests)	100-415 mg/Nm^3 (4 tests)
PM size	98-100% < 10 μm 80-97% < 1 μm	75-87% < 10 μm 45-51% < 1 μm

Notes:
1. Most data reported in the literature are for Orimulsion 100, although there are several data points for Orimulsion 400.
2. Concentrations of all pollutants are as measured, and are not corrected to account for differences in O_2 concentration.
3. Concentrations are measured upstream of any control device.
4. No SO_2 values for fuel oil were reported in the Orimulsion literature. The 1200 ppm value is calculated based on 2% sulfur in the fuel. SO_2 concentrations are strongly dependent upon the amount of sulfur in the fuel.
5. Measured using mini acid condensation sampling (MACS) method.

EPA's pilot-scale results were similar to those reported in the literature in terms of comparison of Orimulsion to heavy fuel oil, with data showing little difference in CO, NO_x, or PM furnace exit concentrations, and smaller particles for Orimulsion than for heavy fuel oil. The pilot-scale data differed most from the full-scale data for NO_x, but were not unreasonable given the difference in combustor system design. The pilot-scale tests provided further valuable confirmation of the similarity between Orimulsion and heavy fuel oil, and also generated samples for use in inhalation toxicity testing. The pilot-scale data were not intended to be directly comparable to full-scale performance data, but were intended to identify fundamental differences between the fuels.

Toxicity Testing
NHEERL conducted tests measuring the pulmonary toxicity in laboratory animals of PM generated by the combustion of Orimulsion 100, Orimulsion 400, and No. 6 fuel oil. Laboratory rats were exposed by intratracheal instillation of different doses of PM from each of the fuels burned in the NRMRL combustion tests, as well as Arizona road dust (ARD) and a saline solution as control measurements. Five biomarkers of pulmonary toxicity or injury (bronchial alveolar fluid [BALF] neutrophil/mL, BALF protein, albumin, lactate dehydrogenase [LDH], and eosinophil/mL) were measured at 24 hours post-exposure. Each sample was ranked according to its lowest observed effect level (LOEL) for each of the five biomarkers. The relative toxicity rankings for each biomarker were:

BALF protein	No. 6 fuel oil > Orimulsion 400 ≥ Orimulsion 100 > ARD = Saline
albumin	No. 6 fuel oil ≥ Orimulsion 100 ≥ Orimulsion 400 > ARD = Saline
LDH	Orimulsion 400 > Orimulsion 100 = No. 6 fuel oil = ARD = Saline
neutrophil	Orimulsion 100 = Orimulsion 400 = No. 6 fuel oil = ARD > Saline
eosinophil	Orimulsion 100 = Orimulsion 400 = No. 6 fuel oil > ARD > Saline

The conclusion drawn by the toxicity tests is that, under the combustion conditions employed in these studies, both Orimulsion formulations generated particulate emissions that were capable of producing significant adverse acute pulmonary toxicity. In addition, particles derived from the combustion of Orimulsion 100 and Orimulsion 400 were found to be very similar to No. 6 fuel oil fly ash particles in their ability to induce acute pulmonary toxicity. Different results are possible for particles from full-scale units with different operating conditions, for animals exposed via direct inhalation rather than instillation, or for health-compromised animals. Tests of toxicity related to exposure by routes other than inhalation, or of ecological toxicity, were not conducted under this study.

Spills

Orimulsion is considered to be a "non-floating" oil. Once spilled, the bitumen fraction of Orimulsion is likely to either sink or remain neutrally buoyant, rather than forming a coherent surface slick, which can have significant implications for contamination of drinking water supplies, since many inlets to drinking water treatment systems are located below the surface of water bodies. Special equipment is required to effectively contain and recover Orimulsion spills in saltwater environments, and such equipment is currently used at shipping terminals where Orimulsion is off-loaded.

Data gaps remain in the understanding of the behavior and fate of Orimulsion spilled in fresh water. This is important because most spills occur at stationary facilities rather than during shipment. As noted in the Orimulsion Technology Assessment Plan, if Bitor does begin to develop U.S. customers at sites accessible only by fresh water, at a site near bodies of fresh water, or at a site where fresh water can be contaminated by a spill, even indirectly, Bitor should be responsible for the research to address the data gaps as they have done for marine environments. Such research does not fall under the Congressional directive for this report, and should not be considered to be EPA's responsibility under that directive. However, since EPA is responsible for responding to spills in certain situations, the Agency should continue to investigate Orimulsion spill behavior and response as appropriate. EPA (in collaboration with the U.S. Coast Guard) has requested the National Academy of Sciences to conduct a study on Orimulsion to evaluate what additional information is required to effectively respond to freshwater spills. EPA is currently conducting smaller studies on spill behavior modeling, and will address the data gaps identified by the NAS as appropriate. EPA should remain aware of any research conducted by others regarding freshwater spill research.

Risk Assessment

The potential ecological risk associated with the use of Orimulsion was evaluated by a panel of independent reviewers chosen by EPA, who examined the work carried out by a U.S. utility to estimate the ecological risk associated with a potential spill in the Tampa Bay, Florida marine environment. The utility-funded study compared a hypothetical spill of Orimulsion 100** to a hypothetical spill of an equal volume of heavy fuel oil. The comparative assessment examined transport and fate of both fuels, including potential effects on shorelines and aquatic biota under a range of different spill locations, seasonal variations, and wind and current conditions.

The independent reviewers agreed with the major conclusion of the Bitor study that a spill of Orimulsion 100 likely poses a similar or lower risk to Tampa Bay biota than does an equivalent spill volume of No. 6 fuel oil. However, the reviewers noted that parts of the assessment, such as risk characterization, population modeling, and impacts to benthic (sea-, river-, or lake-bottom) communities, were identified as assessment topics that could be improved. The reviewers felt that these improvements would enhance the Tampa Bay report, but did not feel that the improvements would impact the report's conclusions. The conclusions of the reviewers may differ for different

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**Orimulsion 100 and Orimulsion 400 differ in the formulation of their respective surfactants and in the use of a magnesium-based compound in Orimulsion 100 that is not found in Orimulsion 400. The two formulations are similar enough with respect to spill behavior that the spill assessment conducted for Orimulsion 100 would be expected be only slightly different if Orimulsion 400 were evaluated. No similar study has yet been conducted for Orimulsion 400.

conditions associated with other combinations of variables such as location, weather conditions, level of fuel use, and diversity and number of biota in the locality.

The review did not examine other factors beyond the scope of the original assessment that may have significant adverse ecological and health impacts, such as physical effects of an Orimulsion spill on biota. In addition, the review examined only the utility-funded assessment, and did not examine other literature on Orimulsion or heavy oil spill behavior, fate, and effects.

A study of cancer risk associated with air emissions from the combustion of heavy fuel oil in electric utility steam generating units was used as the basis for comparing cancer risks due to the use of Orimulsion with those from the use of heavy fuel oil. The original study evaluated the risk to human health associated with exposure to HAP emissions from electric utility steam generating units, and estimated that 0.4 additional incidences of cancer were estimated to be caused by exposure to Ni emissions from all 137 oil-fired plants in the U.S. This value was estimated to be a conservative estimate of the potential cancer risk associated with the use of Orimulsion, based on the Ni emissions from both fuels.

Potential Use of Orimulsion
Orimulsion can be used in applications similar to coal or heavy fuel oil. Orimulsion is readily used in plants designed to use heavy fuel oil, due to the fuels' similar handling and use characteristics. The difference in fuel prices between fuel oil and coal may also favor fuel oil as being more likely to be replaced with Orimulsion. The states with the highest fuel oil use are (in order of consumption) Florida, New York, Massachusetts, Connecticut, and Hawaii, all of which are oil consumers and not oil producers. They are also located on the coast, and may be more suitable markets for Orimulsion than states with high coal consumption.

Previous experience with Orimulsion indicates that conversion to the fuel may require significant changes to existing equipment, including air pollution control systems, fuel supply and handing systems, and boiler internal components.

Chapter 1
Introduction and Background

Orimulsion* is a liquid fossil fuel consisting of an emulsion of 70% bitumen (a naturally occurring heavy petroleum material) from the Orinoco region of Venezuela, 30% water, and a small amount of surfactant (see Chapter 2). In recent years, Orimulsion has been proposed as a fuel to replace either coal or heavy fuel oil in utility power plants throughout the world. However, there has not been a comprehensive evaluation of the fuel by an independent organization that would provide an overview of the fuel, its current and proposed uses, or its potential environmental impact. The objective of this report is to provide such an overview based on the information available in the open literature and from the results of limited testing of the fuel by the U.S. Environmental Protection Agency's (EPA's) National Risk Management Research Laboratory (NRMRL).

Background

Orimulsion was first used commercially in 1991 at two plants in the U.K. and one in Japan. The first commercial use of Orimulsion in North America was in 1994 at New Brunswick Power's Dalhousie Generating Station, located in Dalhousie, New Brunswick, Canada. Since that time, eight other sites have converted to Orimulsion, with several other plants either converting or considering its use. Because of the rapid growth in Orimulsion use, concern over the environmental impacts associated with using Orimulsion has increased. These concerns include environmental exposures of toxic or harmful materials to the environment by accidental spills and by stack emissions and disposal of ash generated by the combustion of Orimulsion.

In the mid-1990s, Orimulsion was proposed as the fuel for one power plant in the U.S., but to date no plant in the U.S. has used the fuel other than in short-term testing. Because of the interest in and concern about using Orimulsion as a fuel for utility and industrial boilers, the U.S. Congress requested that EPA initiate a study to evaluate the environmental impacts associated with using Orimulsion. In Fiscal Year 1998 the Congress added the following language to the Conference Report on Bill H.R. 2158 appropriating funds for EPA operations:

> The conferees are aware that orimulsion, a mixture of bitumen and water, is being considered for generating electricity in the United States. While orimulsion has been used in several countries including Japan, China, Italy and Canada's maritime provinces, it has not been utilized within the United States. Because little is known about the risks associated with the introduction of this new product, the conferees direct EPA to initiate a research activity to provide better scientific data on the qualities and characteristics of this product and the potential environmental impact of its introduction. (U.S. House of Representatives 1997)

In response to this request, NRMRL's Air Pollution Prevention and Control Division (APPCD) led an effort by EPA's Office of Research and Development to prepare a technology assessment plan to evaluate the environmental impacts associated with the use of Orimulsion in utility and industrial boilers (EPA 1999a). This plan was reviewed by an external panel of experts, and revised to address their concerns. The plan's focus is on the air emissions, as it was the panel's opinion that issues associated with spills had been addressed by a number of studies and that a review of these studies could provide the information necessary to adequately determine the environmental impact associated with a spill of Orimulsion in salt water (Freedman et al. 1998).

The Orimulsion Technology Assessment Plan was developed as a three-phase approach to allow results generated during the initial testing to be used as guidance in the later phases. The emphasis of the first phase was on the pilot-scale testing at NRMRL and the toxicology tests using the fly ash generated during those tests. The second phase would expand the emissions testing to include field sampling of full-scale units, preferably sampling the flue gases from both Orimulsion and the

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*Orimulsion is a registered trademark of Bitúmenes Orinoco, S.A.

preconversion fuel (expected to be heavy fuel oil). This phase would also include toxicological tests, with the samples being taken from the field tests instead of the pilot-scale tests. Phase III would expand the field tests and include a more detailed environmental assessment which would include the toxicology data from Phases I and II. Phase I was funded by EPA; however, the need for subsequent phases was deemed to be contingent upon the findings of Phase I.

Phase I of the NRMRL Technology Assessment Plan included four major components. The first of these was a review of the available literature, including a number of test reports made available to NRMRL by Bitor America Corporation (Bitor). The second component was a set of pilot-scale tests to evaluate the basic combustion behavior and emissions characteristics of Orimulsion and a heavy fuel oil* in a single pilot-scale combustor. This approach was intended to allow a comparison of the emissions and combustion performance of both fuels. The third component was a series of toxicological tests to be conducted by EPA's National Health and Environmental Effects Research Laboratory (NHEERL), co-located with APPCD in Research Triangle Park, NC. These tests would evaluate the acute toxicity of the collected fly ash generated by the combustion of Orimulsion and compare it to that of heavy fuel oil. The fourth component was an assessment of the environmental impacts of Orimulsion use, including exposure to fly ash generated by Orimulsion combustion and to Orimulsion spills. This component was conducted by EPA's National Center for Environmental Assessment (NCEA), located in Research Triangle Park, NC (EPA 1999a).

Although spills of Orimulsion into bodies of water pose a potentially significant environmental threat, this topic was determined not to be an area in which research was immediately required. There has been considerable work conducted under the guidance of the International Orimulsion Working Group (IOWG). The IOWG is composed of interested parties from Bitor, the fuel's U.S. marketer, the National Oceanic and Atmospheric Administration, the U.S. Coast Guard, Environment Canada, Fisheries and Oceans Canada, and the Canadian Coast Guard. This work has focused on spill behavior, effects, and response primarily in saltwater (marine) and to a lesser extent in freshwater environments, and has been funded largely by Bitor. A study of non-floating oil spills conducted by the National Research Council (NRC) was recently completed, and also touched on spills of Orimulsion in both freshwater and marine environments (National Research Council 1999). Discussions within EPA, and further confirmed by interagency reviews of the Orimulsion Technology Assessment Plan, concluded that, although there remains a significant gap in the understanding of the behavior, fate, and effects of Orimulsion in fresh water, the bulk of the research in this area should be the responsibility of Bitor rather than of EPA. Further, there are currently no near-term plans for using Orimulsion at sites which would receive the fuel via freshwater routes. Therefore the decision was made to focus this study on air pollutant emissions and rely on existing spill data to provide an understanding of the risks associated with spills of Orimulsion in marine environments. However, this decision did not preclude the potential for further EPA research on Orimulsion to address needs identified by EPA's regulatory offices.

This document reports on the results of Phase I of the Orimulsion Technology Assessment Plan.

Overview of Orimulsion and its Use

Orimulsion is a bitumen-water emulsion produced from bitumen extracted from the Cerro Negro field of the Orinoco Belt of eastern Venezuela (see Figure 1-1). Total Orinoco bitumen reserves have

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*The terms residual fuel oil, heavy fuel oil, and No. 6 fuel oil are used interchangeably throughout this report. Residual fuel oils typically refer to the petroleum products that remain after removal of distillate products from the crude oil. "Bunker C" is also often used as a term to describe residual fuel oil. No. 6 fuel oil is a grade of residual oil that has a Saybolt Universal viscosity range between 900 and 9000 s and requires preheating for handling and burning (Reed, 1998a). Heavy fuel oil can refer to either No. 6 fuel oil or a "heavy" No. 5 fuel oil, and usually (but not always) requires preheating for handling and burning.

been estimated at approximately 1.2 trillion (10^{12}) barrels* (oil equivalent), with 267 billion (10^9) barrels (oil equivalent) in economically recoverable reserves using current technology (U.S. Department of Energy 1998a). These figures compare to 1.02 trillion barrels of world recoverable crude oil reserves, 22.5 billion barrels of U.S. recoverable crude oil reserves, and an energy equivalent of 995 billion barrels of crude oil in U.S. recoverable coal reserves (U.S. Department of Energy 1998b). Orimulsion is produced by a subsidiary of the Venezuelan national oil company Petróleos de Venezuela, S.A. (PDVSA), Bitúmenes Orinoco, S.A. (PDVSA-Bitor), and derives its name from the combination of "Orinoco" and "emulsion." PDVSA is exploring other areas within the Orinoco Belt as possible bitumen extraction sites, and PDVSA-Bitor has long-term plans for three additional Orimulsion production facilities. In 1998, long-term plans estimated exports of Orimulsion to be as high as 20 million tons per year by 2000 (U.S. Department of Energy 1998a). However, those plans have been scaled back, and current plans call for approximately 6 million tons to be exported in 2000 (Garcia 1999).

The primary market for Orimulsion to date has been as a fuel for electric utility boilers, with 3,866 MWe of generating capacity world-wide using Orimulsion as a primary fuel. Plants are currently operating with Orimulsion in Canada, Denmark, Italy, Japan, and Lithuania, and two plants have operated in the United Kingdom (Quig and Woodworth 1997). Orimulsion has replaced both heavy fuel oil and pulverized coal as primary fuels at these plants. The wider price difference between Orimulsion and heavy fuel oil compared to coal makes replacement of fuel oil more economically attractive. Further, most plants designed for using heavy fuel oil can be converted to Orimulsion without major modifications, and many of these plants are located near seaports. The latter consideration is important because Orimulsion is normally transported to plants using ocean-going tankers, with additional transport expense making supply of plants without direct seaport access less cost-effective.

Plans for additional conversions to Orimulsion from other fossil fuels or for new plants have been announced for Italy and possibly in Guatemala (Power Generation 1998). Firms in Korea and Taiwan have also undertaken reviews of the fuel for potential future use (U.S. Department of Energy 1998a). In the U.S., feasibility studies have been conducted on the potential costs of converting to Orimulsion for at least three power plants, but only one utility has sought to convert to the fuel (Energy and Environmental Research Corporation undated, Lentjes Bischoff 1997). Florida Power & Light Company's application for a permit to convert its Manatee Power Plant from heavy fuel oil to Orimulsion was denied in 1998, and as of early 1999 there has not been any further attempt to use Orimulsion in the U.S.

Air Emissions

Air emissions from fossil fuel combustion may be of concern for several reasons. Some compounds emitted into the atmosphere from these sources are considered carcinogenic, while others may lead to different health problems or to unacceptable environmental damage. Acute exposure to elevated levels of a compound may be of concern, while chronic exposures at lower levels may be the primary concern associated with other compounds. These considerations have led to different regulatory approaches to limiting emissions of air pollutants.

Criteria pollutants are those for which National Ambient Air Quality Standards (NAAQS) have been established, and include carbon monoxide (CO), nitrogen dioxide (NO_2), ozone (O_3), sulfur dioxide (SO_2), particulate matter (PM) less than 10 μm in aerodynamic diameter (PM_{10}), PM less than 2.5 μm in aerodynamic diameter ($PM_{2.5}$), and lead (Pb). Nickel (Ni) and magnesium (Mg) are listed along with 187 other compounds and compound classes as hazardous air pollutants (HAPs) under the 1990 CAAAs (Clean Air Act 1990). Vanadium (V) is not listed as a HAP, but [along with other transition metals such as copper (Cu), iron (Fe), Ni, and zinc (Zn)] has been hypothesized as playing a key role in causing acute adverse health effects associated with exposure to $PM_{2.5}$ (Dreher et al. 1996a, 1996b, 1997).

**See Appendix A for conversions to SI units.

Figure 1-1. Orinoco region of Venezuela (adapted from Bitor undated).

Compared to some other fossil fuels, Orimulsion has elevated levels of sulfur, nitrogen, Ni, and V (Mg levels for Orimulsion 100 were also elevated due to the Mg additives that are not in Orimulsion 400). The presence of sulfur in fuels leads to emissions of SO_2, and elevated nitrogen levels contribute to higher emissions of oxides of nitrogen (NO_x). NO_x is composed of NO_2, a criteria pollutant, and nitric oxide (NO), which plays a key role in the formation of O_3 in the presence of ambient concentrations of volatile organic compounds (VOCs) and sunlight. Orimulsion also behaves like other emulsified fuels in producing PM that is largely composed of $PM_{2.5}$. For these reasons, the air emissions generated by the combustion of Orimulsion may be of concern if not properly controlled.

However, as noted above, it is important to compare these emissions with those from other fuels, as Orimulsion will be used in lieu of other fuels and not in isolation. Air pollutants are generated and emitted from the combustion of all fossil fuels, and can be reduced by applying appropriate air pollution control methods and technologies. Therefore it is important to understand the effects on emissions associated with the change in fuel distinct (to the extent possible) from the effects of system design and operation.

It is also important to evaluate Orimulsion emissions both before and after any treatment by pollution control equipment to the extent possible. Measurement of uncontrolled pollutant concentrations from Orimulsion provides a consistent basis for comparison that is not influenced by the different design and performance characteristics of pollution control equipment. Measurement of controlled emissions allows one to evaluate how well current air pollution control technologies are able to reduce emissions generated by the combustion of Orimulsion. If it is not possible to measure emissions both before and after any pollution controls, knowledge of the uncontrolled emissions and the efficiency and applicability of pollution control equipment can be used to estimate controlled emissions.

Spills

Orimulsion has two characteristics that significantly impact its behavior when spilled in water. First, Orimulsion falls into a category of fuels termed by the American Petroleum Institute (API) as "low API oils" (LAPIOs), whose densities are greater than that of fresh water and very close to that of salt water. This characteristic results in a fuel's tending to settle or sink in fresh water and remain

neutrally buoyant in salt water (water containing more than 20 ppt salt). Sinking or settling spill plumes are difficult to track and recover with conventional spill containment and recovery technologies (National Research Council 1999). Second, the presence of a surfactant in Orimulsion and other emulsified fuels prevents the coalescence of hydrocarbon particles, leading to higher particle dispersion and further complicating containment and response measures. Thus, spills of Orimulsion require the use of special equipment and techniques during spill containment and response.

Similar to the air emissions issue, the issue of Orimulsion spills cannot be viewed in isolation, since the transport and use of other liquid fuels (heavy fuel oil in particular) also pose a risk of environmental damage due to spills and subsequent environmental exposure. Understanding changes (both increasing or decreasing) in risk associated with the use of Orimulsion compared to practices that are currently accepted is of greatest importance to objectively evaluating risks associated with use of the fuel. This is true for potential spills as well as for air emissions or other environmental issues related to Orimulsion use.

Objective
The Orimulsion Technology Assessment Plan is designed to address the main issue raised by Congress, that is, to provide better scientific data on the qualities and characteristics of Orimulsion and the potential environmental impact of its introduction. The key questions addressed by this report are:

1. Are the emissions from the combustion of Orimulsion significantly different from those from other fossil fuels, and if so, how?
2. Can the emissions from the combustion of Orimulsion be adequately controlled using existing air pollution control technologies? If not, are there modifications to existing technologies that can be made to adequately control emissions, or are new control technologies required?
3. Is the behavior of Orimulsion during a spill significantly different than the behavior of other fossil fuels, and if so, how?
4. What gaps in understanding the behavior of Orimulsion exist, based on the behavior of other fossil fuels and the known properties of Orimulsion? Are these gaps serious with respect to understanding the potential environmental impacts, and if so, what research should be conducted to address these gaps?

The objective of this document is to answer these questions to the fullest extent possible and to provide appropriate conclusions regarding the use of Orimulsion and how it may impact the environment.

It is not the objective of this report to address possible regulatory requirements or to estimate the costs associated with meeting such requirements. In each case, there are many site-specific factors that are determined by local regulatory requirements and that can significantly impact the cost of converting to Orimulsion. The data and the conclusions presented in this report should not be considered as endorsing or discouraging the use of Orimulsion. The conclusions of this report cannot be considered as identifying specific approaches for meeting regulatory requirements.

Approach
The approach taken in addressing the above questions was to conduct independent testing of Orimulsion to the greatest extent possible and to compare the results from those tests to existing data. Substantial data on the behavior of Orimulsion in combustion applications and in spills have been presented in the open literature, and these data were used where appropriate.

Most of the data in the open literature have been collected under test programs funded by Bitor or utility companies interested in using Orimulsion. Although concerns have been expressed regarding the objectivity of these data, this information can and should be used in developing conclusions as to the environmental impacts of Orimulsion use if the data are of sufficient quality to make such use

appropriate. Determining whether these data are of sufficient quality to be used is a matter of technical judgement, and a discussion of data quality for results generated by EPA under this program and of those in the literature will be discussed in detail in the chapter on Quality Assurance.

The use of data from the literature allows a broader range of experience to be evaluated in determining the behavior or Orimulsion. While it may be desirable to conduct a completely independent set of tests ranging from bench to full scales over a range of conditions, it is much more effective to evaluate results from a variety of sources, critically review those results, and incorporate the data that are determined to be suitable for use. The factors that determine whether data from the literature should be used include: the quality assurance data reported in the test reports or articles (are replicates, calibrations, and similar measurements included?); the consistency of the results with other Orimulsion tests and with tests of other fossil fuels (do the results make sense in relation to other results?); and the consistency of the results with fundamental physical and chemical behavior (do the results make sense in relation to what is expected based on an understanding of other fuels with similar physical and chemical characteristics?). Finally, even those data from the literature that appear to be inconsistent with other results and with expected behavior should be noted. In such cases, these "outlier" results may indicate different measurements, different processes, incorrect results, or in some cases an unexpected result may indicate important, but previously unrecognized, changes in fundamental behavior. Whatever the reason for the inconsistency, it is important to identify such results and bring the inconsistency to the notice of the technical community.

Report Structure
In Chapter 2, this report discusses the general properties and characteristics of Orimulsion. Chapter 3 presents a review of previous work, including pilot- and full-scale emissions tests of Orimulsion combustion and comparison to emissions from heavy fuel oil. Chapter 4 presents the experimental approach and equipment used in the pilot-scale combustion tests conducted at APPCD. Chapter 5 presents the results of the APPCD pilot-scale tests. Chapter 6 presents the results of the toxicity testing conducted for this project. Chapter 7 addresses spills, and Chapter 8 reviews an environmental risk assessment conducted to evaluate the potential environmental impact of a spill of Orimulsion in a saltwater environment. Chapter 9 compares Orimulsion to other fossil fuels from an environmental perspective. Chapter 10 presents the quality assurance procedures and measures taken during this project, and Chapter 11 presents conclusions and recommendations drawn from this study. References are given in Chapter 12, and Appendices providing unit conversions, raw data, and detailed technical reports follow the report chapters.

Chapter 2
Properties and Characteristics of Orimulsion

Background
Orimulsion fits into the general category of emulsified fuels, which broadly includes emulsified fuel oils, coal-water slurries, and coal-oil slurries. Orimulsion is typical of an oil-in-water emulsion, meaning that the water is the continuous phase and the Orinoco bitumen is the dispersed phase. This chapter will discuss the properties and characteristics of Orimulsion that influence its combustion behavior and the emissions generated by its use in combustion systems. To better understand the behavior of Orimulsion in combustion systems, properties of emulsified fuels (particularly emulsified heavy fuel oils) and their combustion behavior in general will first be discussed, followed by a more detailed discussion of Orimulsion as a fuel.

Properties of Emulsified Fuels
Hydrocarbon fuels emulsified with water* have been studied for many years as means to improve operating efficiency and reduce combustion-generated pollutant emissions (Dryer 1976). The addition of water can increase the performance of internal combustion systems such as piston engines and gas turbines by taking advantage of the water's expansion to steam during heating. The lower combustion temperatures associated with water addition can also reduce emissions of nitrogen oxides (NO_x). The presence of water vapor can also enhance the production of hydroxyl radicals, which increases the reaction rate of carbon monoxide (CO) to carbon dioxide (CO_2), promoting more rapid completion of the combustion process (Dryer 1976).

Combustion Behavior
Early water addition tended to be in the form of water injection into the engine cylinder or turbine combustor can. Mixing the water and fuel (usually distillate oil) together allowed a single injection, but also required the use of a surfactant to ensure the mixture did not separate prior to injection. Most oil-water emulsions used as fuels tend to be water-in-oil emulsions, in which the oil is the continuous phase and the water forms the dispersed phase. These emulsions exhibit physical behavior that also contributes to improved performance through the phenomenon of "micro-explosions." Dryer (1976) discussed the work of Ivanov and Nefedov (1962) which postulated that when heated, the small droplets of water (surrounded by a fuel oil of higher boiling point) would rapidly and disruptively vaporize and expand, shattering the original emulsion droplet into many smaller droplets. Further work by Dryer et al. (1976) has demonstrated this secondary atomization resulting in very fine fuel droplets that can devolatilize and burn out more quickly and more completely than the much larger fuel droplets produced by mechanical atomization. The findings of Ivanov and Nefedov were summarized as follows (Dryer 1976):

> "1. Emulsified fuels burn faster than anhydrous ones.
> "2. Water in emulsified fuels does not impair, but improves the combustion process, owing to the additional simultaneous breaking of the droplets, and to a better mixing of the burning substances in air.
> "3. The reduction of the combustion time of emulsified fuels has a favorable influence on the burning of sooty residue, thus improving the completeness of combustion and reducing the deposition of soot (scale) on the working surfaces."

The secondary atomization and the presence of water allow heavy fuels to be combusted at lower peak temperatures and lower excess air levels than would be possible with non-emulsified or "neat" fuels, often with increased fuel burnout. Studies of emulsified fuel combustion in practical systems indicated that water-in-oil emulsions could reduce PM (as measured by smoke number) at constant

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*Emulsified fuels are fuels that are composed of a mixture of a solid and liquid phase, where the solid phase is suspended as particles in the liquid phase.

excess air, with little change in either CO or NO_x (Hall 1975, 1976). Using an emulsified oil allowed an operator to reduce excess air to a point where the smoke number was equal to that under baseline excess air using neat fuel oil, thereby resulting in reductions of NO_x without increases in PM. These results were verified in two separate studies of emulsified heavy fuel oil and two emulsified light fuel oils in a small commercial boiler (Miller 1996, 1998).

Impact on Boiler Efficiency

The disadvantage to using oil-water emulsions is the additional mass of water that is heated and carried out of the boiler, representing an energy loss from the perspective of boiler efficiency. In addition, the change in heat release characteristics due to the added water may also have significant impacts on where within a boiler the heat transfer occurs. For instance, a slower heat release rate within the boiler may shift a substantial portion of heat transfer from the radiant waterwalls and superheater to the convective section. Changes in heat transfer surface areas may be required to minimize the overall impact on boiler operation. The impact on boiler efficiency depends largely upon the amount of water that is added to the oil.

One method of determining boiler efficiency is the heat loss method as defined by the American Society of Mechanical Engineers (ASME) in their Performance Test Code (PTC) 4.1 (American Society of Mechanical Engineers 1991). This method relies on measurements of the input energy (the energy flowing into the system with the fuel and air) and energy losses; i.e., energy that is not absorbed by the steam. Such losses include energy carried out of the system by the flue gases and unburned fuel, energy radiated from the boiler skin to the surroundings, and energy escaping the boiler from leaks. The ASME PTC 4.1 defines efficiency through the heat loss method as:

$$\eta = 100\% - \left(\frac{\text{Heat losses}}{\text{Heat in fuel} + \text{Heat credits}} \right) \times 100\% \qquad (2\text{-}1)$$

where heat credits involve energy inflow through the boiler feedwater and combustion air. The heat-in-fuel term is the product of the fuel's higher heating value and the flow rate of the fuel to produce energy per unit time.

The major heat loss is through the sensible heat in the flue gases; however, other heat losses may also be significant, depending upon the operating characteristics of the particular boiler. In addition to flue gas heat loss, energy may also be lost through leaks of boiler water or combustion gases; the presence of CO, unburned hydrocarbons, and/or unburned carbon in the flue gases; or the presence of water in the fuel. The total heat loss is simply the sum of those losses, calculated in Btu/hr.

The changes in heat losses for an oil-water emulsified fuel will be most pronounced in the losses through the sensible heat and the losses through the presence of water in the fuel. The heat loss through the sensible heat in the flue gases is a product of the flue gas flow rate, specific heat, and difference in temperature from ambient. Thus, at a given exit temperature, as more mass flows out of the boiler due to the added water, the more heat is lost through the sensible heat and the lower the thermal efficiency.

The heat loss due to the moisture in the flue gases is the sum of the loss associated with the moisture in the fuel and the loss associated with the conversion of hydrogen to water in the combustion process. For oil-water emulsified fuels, the major change to the thermal efficiency is due to the increased moisture in the fuel. This loss is calculated from

$$L_{MF} = f_{MF} \left(h_{WG} - h_{ref} \right) W_F \qquad (2\text{-}2)$$

where L_{MF} is the heat loss due to moisture in the fuel, f_{MF} is the percent moisture content of the fuel, h_{WG} is the enthalpy of the water vapor in the flue gases at the stack temperature and vapor partial pressure (generally assumed to be 1 psia) in Btu/lb, h_{ref} is the enthalpy of saturated liquid water at the

reference temperature (68 °F) in Btu/lb, and W_F is the flue gas mass flow rate in lb/hr. h_{WG} and h_{ref} are determined from standard ASME steam tables. As was the case for the sensible heat loss, the change in loss due to moisture in the fuel is directly proportional to the change in the percent moisture content of the fuel.

A 30% water content in an emulsified heavy fuel oil has been shown to reduce boiler thermal efficiency by 2-3%, compared to the same neat heavy fuel oil with a moisture content of less than 0.05% (Miller 1998).

Fuel Handling
Fuel handling characteristics can impact emissions of pollutants in combustion systems, as poor nozzle atomization or unsteady flows can lead to poor burner performance and higher emissions of carbon monoxide (CO), oxides of nitrogen (NO_x), and unburned hydrocarbons. Therefore, it is important to be aware of the fuel handling characteristics of emulsified fuels that may lead to the above problems.

Properties of Orimulsion
Orimulsion is an emulsion of bitumen and water, with the bitumen being the dispersed phase and water being the continuous phase. The bitumen is produced in Venezuela's Orinoco Belt, degassed, dehydrated, and desalinated and emulsified in water. An emulsifying agent is added to stabilize the emulsion. The term "Orimulsion" is derived from the combination of "Orinoco" and "emulsion."

The bitumen used in Orimulsion is taken from wells in the Cerro Negro field in the Orinoco belt of eastern Venezuela. Bitumen is a naturally occurring hydrocarbon with a viscosity greater than 10,000 mPa-s at ambient temperature. Table 2-1 presents typical properties of the Cerro Negro bitumen.

Much of the information on Orimulsion properties and handling in this section is taken from the Orimulsion Design and Operations Manual, Version 4.0 prepared by Bitor Europe (Bitor Europe, 1994) and from the Bitor America report, Physical and Chemical Characterization of Orimulsion-100 Fuel, its Constituents and ByProducts of Combustion (Bitor America 1997).

Table 2-1. Typical properties of Cerro Negro bitumen (Bitor America 1997).

Property	Value	Property	Value
Carbon, %[1]	85.3	° API	8.0
Hydrogen, %	9.7	Viscosity, mPa-s at 25 °C	8×10^4 - 10^5
Nitrogen, %	0.54	Density, kg/m^3 (at 15 °C)	1.019
Oxygen, %	0.30	Gross heating value, MJ/kg	42.8
Sulfur, %	4.04	Flash point, °C	120
Ash, %	0.12	Pour point, °C	38
Sodium, ppm	40	Saturates, %	10.7
Vanadium, ppm	440	Aromatics, %	58.0
Nickel, ppm	110	Resins, %	19.3
Iron, ppm	12	Asphaltenes, %	11.9

1. Percentages are weight percentages, unless otherwise noted.

Fuel Composition

There are currently data on two different formulations of Orimulsion, that differ with respect to the surfactant used and to the use of a magnesium (Mg) additive to minimize boiler surface corrosion. The original formulation was generally referred to as Orimulsion. When the new formulation was introduced in late 1998, the two formulations were distinguished by referring to the original as Orimulsion 100 and the new as Orimulsion 400. Bitor has replaced all Orimulsion 100 with Orimulsion 400 and no longer produces the original formulation. The terms 100 and 400 refer to the Bitor nomenclature for the emulsifying agents used in the different formulations. No Orimulsion 200 or Orimulsion 300 have been produced.

Orimulsion 100 consisted of approximately 70% by weight of Orinoco bitumen, 29.8% water, 0.2% nonyl phenol ethoxylate as the surfactant and approximately 350 ppm (Mg equivalent) of magnesium nitrate. Orimulsion 400 consists of approximately 70% Orinoco bitumen, 29.8% water, and 0.13% tridecylalcohol ethoxylate and 0.03% monoethanolamine as surfactant.

Orimulsion 100 consisted of bitumen droplets with a single mode at approximately 17-18 μm in diameter, with a median size of 10-15 μm in diameter, and with less than 1% of droplets larger than 150 μm in diameter. In some instances, the median droplet size and the percent of droplets larger than 150 μm may have increased under certain operating conditions, but this change was not linked to any changes in boiler performance or operational problems. Orimulsion 400 is produced with a bimodal bitumen size distribution, with the modes at approximately 8 μm and 24 μm in diameter. The bimodal distribution allows for closer packing of the bitumen droplets and also results in lower viscosity of the emulsion. There have been some suggestions that the bimodal distribution also results in a "staging" effect in which the smaller droplets burn out more quickly than the larger droplets, resulting in lower NO_x emissions and better burnout.

The composition of both Orimulsion formulations are primarily dependent upon the composition of the Orinoco bitumen from which they are produced. The bitumen is mixed with water to create an emulsion of approximately 30% water and 70% bitumen, with small amounts of the emulsifying agent. The Orinoco bitumen is generally high in sulfur (S), vanadium (V), and nickel (Ni), and therefore Orimulsion also has high contents of these elements. Table 2-2 presents typical values and ranges of Orimulsion 100 composition, including several trace elements (Bitor Europe 1994). In addition, Orimulsion also contains several radioactive elements. Table 2-3 presents values of radioactive elements found in Orimulsion (Bitor America 1997).

Fuel Handling

As with any emulsion, Orimulsion requires care in handling to ensure the bitumen and water phases remain uniformly dispersed. Extremes of temperature, excessive shear, or contamination may result in instabilities in the emulsion. The types of instabilities that can occur are illustrated in Figure 2-1. An emulsion that does not remain uniform can lead to high levels of water passing through a burner followed by high levels of hydrocarbons, which in turn can result in poor burner performance and higher pollutant emissions.

Temperature

The effectiveness of the surfactant to maintain a stable emulsion diminishes at temperatures over 175 °F (80 °C). The emulsion begins to deteriorate at temperatures over 210 °F (100 °C) and is completely destabilized at temperatures over 250 °F (120 °C). Although freezing has not been found to cause destabilization of the emulsion, Bitor recommends maintaining the temperature of the fuel above 40 °F (5 °C). Recommended storage temperature for Orimulsion is 85 °F (30 °C). Because of the fuel's sensitivity to high temperatures, Bitor does not recommend the use of steam heating coils, as the contact temperature of the heating coils can result in local temperatures well above the recommended values.

Shear

Although the Orinoco bitumen exhibits Newtonian fluid behavior, Orimulsion does not. Orimulsion

Table 2-2. Typical values and ranges of Orimulsion 100 properties and constituents (Bitor Europe, 1994).

Property or Constituent	Typical Value	Typical Range
C, %[1]	60	55-62
H, %	7.3	7-7.5
S, %	2.7	2.4-2.9
N, %	0.5	0.4-0.55
O, %	0.2	0.18-0.6
V, ppm	300	270-340
Ni, ppm	65	60-70
Na, ppm	30	15-50
Mg, ppm	350	300-450
Cr, ppm	1.1	NA[2]
Fe, ppm	13	NA
Chloride, ppm	92	NA
Ash, %	0.2	0.12-0.25
Water Content, %	29	27-30
Specific gravity at 15° C	1.0113	NA
Average droplet size, μm	10	8-15
Droplets > 150 μm, %	0.7	0.5-1.5
Gross heating value, 10^6 Btu/lb (MJ/kg)	12,860 (29.9)	12,480-13,340 (29-31)
Net heating value, 10^6 Btu/lb (MJ/kg)	11,870 (27.6)	11,620-13,340 (27-29)

1. Percentages are weight percentages, unless otherwise noted.
2. Not available.

must be pumped so as to avoid high shear regimes to minimize any separation or deterioration of the emulsion. Bitor recommends limiting shear rates to less than 500 s^{-1} and velocities to less than 10 ft/s (3 m/s). Because the emulsion is better able to resist degradation from shear at lower temperatures, it is also recommended that fuel lines be maintained at temperatures less than 120 °F (50 °C).

The above limitations result in use of fuel heating systems that do not use steam, which can heat the fuel to temperatures substantially higher than the recommended level in the near vicinity of the heating coil. In addition, it is also recommended that screw pumps be used and that pump speeds be maintained at 1800 rpm or less for Orimulsion 100 and 3000 rpm or less for Orimulsion 400. It is also recommended that fuel recirculation be avoided, and that fuel flow control be based on pump speed rather than on the throttling of control valves, again to avoid high shear situations in fuel lines.

Flow measurements should not be taken with devices using orifice plates or venturis, but non-intrusive, positive displacement, or turbine meters should be used instead to minimize regions of high shear inside the fuel lines.

Table 2-3. Radioactive elements present in Orimulsion (Bitor America 1997).

Isotope	pCi/g
Cobalt 60	< 0.1
Cesium 137	< 0.1
Uranium (natural)	< 0.1
Radium 226	0.1
Radium 228	0.6
Thorium 230	0.5
Thorium 232	0.1
Thorium 228	0.2
Lead 210	0.1
Polonium 210	0.1
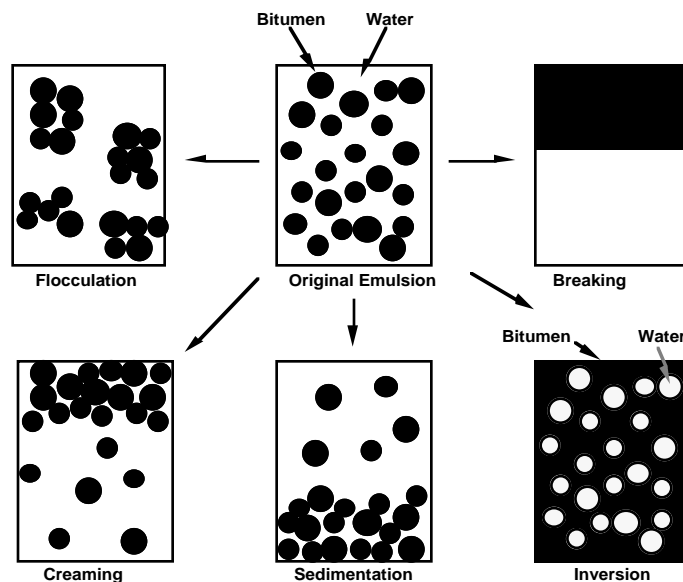
Figure 2-1. Types of instabilities in bitumen-in-water emulsions (Bitor Europe 1994).

Contamination

Orimulsion is not compatible with other fuel oils, although contamination with small quantities (< 5% by weight) of heavy fuel oils has not resulted in destabilization of Orimulsion 400. However, distillate fuel oils and solid matter such as sand or rust may reduce Orimulsion stability. High paraffinic materials are immiscible in Orimulsion, and contamination with such materials can lead to filter plugging. Water can be used to clean Orimulsion from fuel lines or tanks, as Orimulsion is designed to mix with water.

Evaluating Environmental Issues Associated With Orimulsion Combustion

The focus of this report is on emissions and control of air pollutants generated by the combustion of Orimulsion in boilers and furnaces. While spills of Orimulsion into water bodies and generation of

wastewater and solid residues are also important topics to consider when evaluating the environmental impact of Orimulsion use, those issues are beyond the scope of this report. In evaluating environmental issues associated with Orimulsion use in combustion systems, it is the differences between Orimulsion and other fuels that are most critical, since Orimulsion will be used in lieu of other fuels. Such an evaluation is most useful when one looks at the impacts of Orimulsion compared to the fuel or fuels most likely to be displaced by it. This approach is relatively simple when a conversion is made that does not significantly change the output of plants other than the one being converted, but this is the most simple case. If, for example, an electrical generating station converts from firing only heavy fuel oil to firing only Orimulsion and the total amount of electricity produced in each instance does not change over the time periods measured, then the total mass emissions from heavy fuel oil combustion can be directly compared to those from the use of Orimulsion. However, if the output of the plant changes substantially, then the issue becomes more difficult to evaluate.

Consider the case where an electrical generating station converts from firing only heavy fuel oil to firing only Orimulsion, but doubles its output of electricity.** Orimulsion displaces the full amount of heavy fuel oil use at the plant, but also displaces an unknown amount of other fuels that would have been used to generate the remaining electricity at other plants. This electricity may have been produced by the combustion of coal, distillate or heavy fuel oil, natural gas, biomass, or from other sources that do not rely on combustion, such as hydro or nuclear power. The particular fuel or fuels displaced will depend upon the relative costs of power generation at the other available plants, and will change as electricity demand and plant availability change. In general, it would be expected that electricity generated by firing Orimulsion would displace the most expensive fuel, but the specific decision as to which fuel is displaced is a complex decision influenced by factors such as plant availability, pollutant emissions, and maintenance of transmission system reliability.

It is therefore speculative at best to try to estimate the environmental impacts associated with firing Orimulsion on a national or regional basis. One can, however, estimate the impacts of converting an individual plant to Orimulsion from a different fossil fuel. Therefore, this report will focus on the direct differences in environmental impacts due to converting from one fuel to Orimulsion at individual plants.

It is important to note that all fossil fuel combustion results in some impact to the environment, and that the impacts associated with Orimulsion use may be less than the impacts associated with a different fuel. However, the environmental impacts of coal, oil, and natural gas have been studied for many years, and the unknown quantity in this report is the possible impact associated with Orimulsion use.

Air Emissions
The most apparent air emissions issues associated with the combustion of Orimulsion are those arising from the composition of the fuel. Compared to many heavy fuel oils, Orimulsion exhibits increased levels of S, Ni, and V. Increased levels of Mg were also likely with Orimulsion 100 due to the addition of Mg-based compounds for minimizing boiler surface corrosion. Although Orimulsion 400 does not inherently contain an Mg-based additive, boiler operators may inject such additives for corrosion control (this is a relatively common practice when using heavy fuel oils). Because of the increased concentrations of these compounds in Orimulsion, it would be expected that emissions of these compounds and their oxides are likely to be higher when using Orimulsion than when using heavy fuel oil.

It is a simple procedure to calculate the emissions of SO_2, Mg, Ni, and V from the combustion of

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**This discussion does not consider regulatory actions such as the impacts of a "major modification," but is rather intended to emphasize the complexity of determining actual environmental impacts where Orimulsion use may displace other fuels. Issues associated with regulatory actions and requirements are outside the scope of this report.

Orimulsion, since the fuel is the only significant source of those compounds. Mass emission rates (in $lb/10^6$ Btu) of Mg, Ni, and V can be determined by simply dividing the concentration of the individual compounds (in ppm or μg/g) by the energy content of the fuel per unit mass:

$$M_i = c_i \div E \qquad (2\text{-}3)$$

where M_i is the mass emission rate of compound i per unit energy (in $lb/10^6$ Btu), c_i is the concentration of compound i in ppm or μg/g, and E is the energy content of the fuel in Btu/lb.

Likewise, the SO_2 emission rate can be calculated by similar means, but taking into account the additional mass of the oxygen (O_2) required for combustion of the S to SO_2:

$$M_{SO2} = \left(2 \times 10^6 \times c_s\right) \div E \qquad (2\text{-}4)$$

where M_{SO2} is the mass emission rate of SO_2 in $lb/10^6$ Btu and c_s is the fraction of S in the fuel (measured on a wet or as-fired basis). The factor 2 accounts for the fact that the molecular weight of S is 32 and the molecular weight of SO_2 is 64, and the factor 10^6 converts from lb/Btu to $lb/10^6$ Btu.

Predicting emissions of other combustion-generated pollutants is not as straightforward, as they are significantly impacted by the combustion conditions in the boiler. For instance, NO_x formation depends upon the mixing of the fuel and the air, the amount of nitrogen in the fuel, and the peak temperatures reached in the flame. Orimulsion tends to have somewhat higher levels of nitrogen in the fuel, but also has lower flame temperatures, resulting in relatively little change in NO_x emissions when compared to heavy fuel oil.

CO emissions strongly depend upon the amount of O_2 available for completion of the combustion reactions. The small size of the bitumen droplets in Orimulsion allows boilers to operate with less excess O_2 without significant increases in CO, compared with firing heavy fuel oil or pulverized coal. This is because the time required for devolatilization and burnout of the bitumen particles is short due to the small droplet size.

PM emissions can also be dependent upon the combustion conditions, particularly for fuels that have relatively low ash contents. If combustion conditions are poor, increased PM emissions are expected because of increases in unburned carbon or the formation of soot. The small bitumen droplet size and the presence of water in the combustion zone tend to minimize the unburned carbon fraction when burning Orimulsion, and the water tends to assist in suppressing the formation of soot. In addition, the high levels of V in the fuel also acts as a catalyst for improved carbon burnout, further promoting the conversion of the carbon in the fuel to carbon dioxide (CO_2).

The "microexplosions" that characterize emulsified fuels assist in promoting carbon burnout and combustion efficiency, but also result in the formation of very small fuel particles. This behavior, in combination with the small bitumen droplet sizes of Orimulsion, promotes the formation of submicron particles (particles with aerodynamic diameters < 1 μm). For fuel oils, high carbon burnout results in the release of inherently bound metals that form submicron particles through nucleation, condensation, and coagulation mechanisms. In addition to their small size, these particles also tend to contain high levels of metals and sulfur (Linak et al. 1999). Similarly, the PM generated by the combustion of Orimulsion is expected to be characterized by high percentages of submicron particles.

The presence of V in Orimulsion not only affects carbon burnout, but also acts as a catalyst for the formation of SO_3 in higher levels than for other high S fuels that do not have such high levels of V. SO_3 emissions are of concern for several reasons. First, SO_3 is difficult to capture, since it acts as a particle in flue gas desulfurization (FGD) systems and as a gas in particulate capture systems.

Second, SO_3 forms acid aerosols in the stack plume, adding to the total particle emissions of a plant. Finally, SO_3 emissions tend to form visible plumes that can have a significant impact on the public's perception of how well a plant is controlling emissions.

Solid Residues

In addition to the direct emissions of pollutants to the atmosphere, the combustion of fossil fuels often generates solid residues that require disposal. In particular, boilers that use particle control equipment can collect large quantities of fly ash. In some instances, fly ash can be used in production of cement or other building materials. In cases where disposal is necessary, the trace element content of the ash becomes important. Table 2-4 presents the concentrations of metals, halogens, and radioactive elements measured in fly ash generated by Orimulsion combustion. These results, reported by Bitor America (1997), show that Orimulsion fly ash has detectable levels of lead, nickel, vanadium, and the radioactive elements lead 210, thorium, and natural uranium.

In characterizing solid residues for disposal suitability, an important measure is the toxicity characteristic leaching procedure (TCLP), which follows a standard EPA procedure (EPA 1997). TCLP values for As, Ba, Cd, Cr, Hg, Se, and Pb in Orimulsion 100 fly ash were reported as significantly less than the acceptance criteria presented in the Resource Conservation and Recovery Act (RCRA), and in the same range as TCLP values for coal fly ash (Bitor America 1997), as shown in Table 2-5.

Table 2-4. Metals and radioactive elements present in Orimulsion fly ash (Bitor America 1997).

Element	Concentration (µg/g)	Element	Concentration (pCi/g)
Arsenic	< 0.5	Lead 210	0.4
Barium	< 5	Radium 226	< 1.2
Cadmium	< 5	Radium 228	< 1.9
Chromium	< 5	Total Thorium	4.0
Lead	34	Uranium (natural)	0.9
Mercury	< 0.02		
Nickel	25980		
Selenium	< 0.2		
Silver	< 5		
Vanadium	90730		

Table 2-5. Toxicity characteristic leaching procedure (TCLP) results for Orimulsion 100 and coal fly ashes (Bitor America 1997).

Metal	RCRA Criterion (mg/L)	Orimulsion 100 fly ash (mg/L)	Coal fly ash (mg/L)
Arsenic	5	BDL[1]-0.64	BDL-2.68
Barium	100	BDL-0.66	0.11-1.61
Cadmium	1	BDL-0.05	BDL-0.58
Chromium	5	0.62-1.6	BDL-4.64
Lead	5	BDL-1.01	BDL-2.94
Mercury	0.2	BDL-0.04	BDL
Selenium	1	BDL-0.13	BDL-0.15

1. Below detection limit

Chapter 3
Review of Previous Orimulsion Combustion Research and Demonstration

Considerable work has previously been conducted to evaluate Orimulsion's combustion behavior at different scales, from fundamental combustion studies to long-term operational testing. Fundamental combustion and analysis studies, pilot-scale testing, and full-scale demonstrations and operations have been reported in the technical literature, conferences, and trade magazines. In addition, there are a number of internal company reports and studies that have been made available to EPA as part of its efforts to evaluate the environmental effects of Orimulsion use. Many of these have been summarized in a recent review paper (Miller and Srivastava 2000). There are also several references describing Orimulsion studies and applications that have been posted to the World Wide Web. This chapter will discuss the studies that have been done related to the combustion and gasification of Orimulsion, primarily as it relates to air emissions, but with some discussion of wastewater and solid waste disposal as well.

A number of overview papers have been presented that provide basic information about Orimulsion and how it compares to other fuels, what modifications are required to use it, and issues of cost associated with conversion of units to Orimulsion use (Olen 1998a, Quig and Woodworth 1997). Some of these papers do not have detailed information concerning emissions, but rather provide more general information about the fuel, combustion and emissions characteristics, and where it is being (or has been) used.

The majority of reported results are for Orimulsion 100. In some respects, such as for fundamental combustion behavior, little difference is expected between Orimulsion 100 and Orimulsion 400. For issues such as formation of PM and NO_x, predicting the effect of the change in Orimulsion formulation is more difficult. Where data are presented, a distinction is made between Orimulsion 100 and Orimulsion 400. In cases where the text discusses Orimulsion use in general, no distinction is made between the two formulations.

Fundamental Studies

Several studies of the fundamental combustion behavior of Orimulsion have been carried out over the past ten years, primarily at the University of Leeds. Drop tube reactor studies conducted by Williams and Pourkashanian (1987) on bitumen-in-water mixtures concluded that the mixtures exhibited combustion characteristics that were better than coal-water slurries but worse than medium fuel oil, as measured by ignition temperature, maximum fuel droplet temperature, flame lifetime and measured burning rate. The bitumen-in-water mixture was different than the Orimulsion produced currently, but used the same Orinoco bitumen and roughly the same water content. This study concluded that the bitumen-in-water mixture would produce a flame that was more stable than a flame using coal-water slurry as the fuel (Williams and Pourkashanian 1987).

Results of a study of single droplets in a drop tube reactor were reported by Marcano et al. (1991). In these experiments, Orimulsion, Orinoco bitumen, and medium fuel oil, and a hard-bitumen-in-water emulsion were tested (Orinoco bitumen is considered a soft bitumen). The Orimulsion exhibited lower internal temperatures during combustion than the other fuels due to the presence of the water in the fuel. The lower temperatures are believed to lead to the lower emissions of NO_x noted when using Orimulsion. The study concluded that Orimulsion behaved similarly to the fuel oil, while the hard-bitumen-in-water emulsion exhibited behavior that was between the fuel oil and coal-water slurries (Marcano et al. 1991).

This similarity between Orimulsion and heavy fuel oil was further demonstrated by Hampartsoumian et al. (1993) in their study of the burning rate of heavy fuel oil and Orimulsion chars. This study found that the burning behavior of Orimulsion chars was very similar to that of heavy fuel oil, with Orimulsion exhibiting slightly more reactivity than the heavy fuel oil.

Maki and Miura (1997) developed a computer simulation of Orimulsion pyrolysis that calculated a distribution of pyrolysis products. These products may be combustion process intermediate products, and the simulation may provide data for the development of further models of Orimulsion combustion. A two-step model was developed, using a relatively fast primary reaction and a slower secondary gas phase reaction. The simulation modeled a decomposition of the gas phase products to methane (CH_4) and inorganic materials, and a solid phase decomposition to coke.

In addition to the work conducted to evaluate the fundamentals of Orimulsion combustion, research has been conducted in the area of fuel analysis, primarily to determine content of trace metals such as Fe, Mg, Na, Ni, and V (Platteau and Carrillo 1995, Kamiura et al. 1996).

Pilot-Scale Testing
Pilot-scale tests have been conducted at several facilities to evaluate Orimulsion's combustion performance, different burner designs for Orimulsion use, and the use of Orimulsion as a reburning fuel.

Combustion Performance
Test results of Orimulsion 100 combustion performance on a test rig using a single full-scale burner were reported in 1996 (Allen and Beal 1996). These tests evaluated CO, NO_x, and PM emissions as a function of stack O_2 levels for both heavy fuel oil and Orimulsion 100. Uncontrolled CO emissions were lower for Orimulsion 100 at O_2 levels of less than 0.8%, but were lower for heavy fuel oil at higher O_2 levels. NO_x emissions were consistently lower for Orimulsion 100 than for heavy fuel oil, with the lower flame combustion temperatures being attributed for most of the difference. PM emissions were consistently and significantly higher for Orimulsion 100 than for heavy fuel oil, but whether a portion of the PM was due to SO_3 aerosols is not reported. Figure 3-1 shows the CO, NO_x, and PM results reported in this study. The authors also noted that Orimulsion had a higher reactivity, and therefore better combustion properties, than the heavy fuel oil tested (Allen and Beal 1996).

A different burner was tested using Orimulsion 100 and heavy fuel oil on the same test rig as above. The burner was the same as that used in the Dunamenti Power Station operated by the Hungarian Power Company. The emissions results from the tests are presented in Table 3-1. These results are similar to the emissions measured in the tests above, with CO emissions slightly higher for Orimulsion 100 than for heavy fuel oil under the reported conditions, and with NO_x being approximately 20% lower for Orimulsion 100 than for heavy fuel oil. Interestingly, the PM emissions for Orimulsion 100 were less than 40% of the PM emissions for heavy fuel oil, but the PM content as determined by Bacharach smoke number would indicate higher emissions for Orimulsion 100. However, the report noted that the smoke number samples appeared yellow in color, and suggested that this was due to very high levels of sulfates or SO_2 captured on the filter when burning Orimulsion. The report stated that the higher smoke number is due primarily to the higher sulfur content. However, the significantly higher sulfur content of Orimulsion 100 compared to heavy fuel oil was considered to result in either increased formation of sulfate particles in the stack plume or increased stack emissions of SO_3 aerosols (Barta et al. 1996).

The tests of the Hungarian Power Company burner also noted that the Orimulsion flame was not only cooler than the heavy oil flame, but also was longer than the heavy oil flame. This may account for the higher CO emissions in the test rig, which will have less volume for the fuel to complete combustion. The report suggested that the lower measured Orimulsion PM emissions may have been due to deposition of ash in the flame tunnel, since mass balance calculations would predict PM emissions of approximately 500 mg/Nm^3, roughly 20% higher than those measured from heavy fuel oil (Barta et al. 1996).

Tests were also conducted in Canada on a fuel very similar to Orimulsion (Wong et al. 1989, Whaley et al. 1991). A water-continuous emulsion of western Canada bitumen was tested by the CANMET laboratories of Energy, Mines, and Resources Canada in the late 1980s. This fuel was nominally composed of 35% water and 65% bitumen. No information was provided as to the use of surfactants
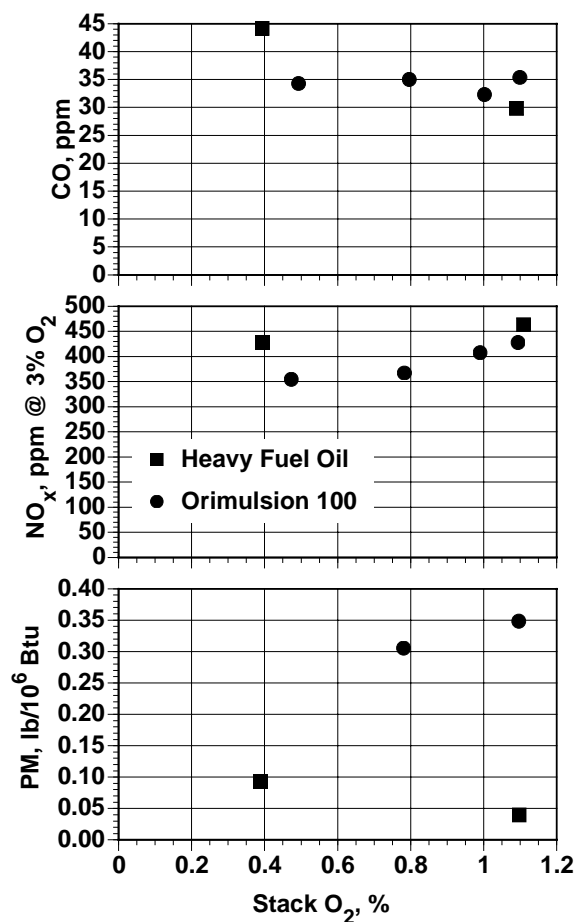
Figure 3-1. Emissions of CO, NO$_x$, and PM measured during pilot-scale tests of Orimulsion 100 combustion (Allen and Beal 1996).

Table 3-1. Flue gas composition for pilot-scale tests using a burner from Dunamenti Power Station (Barta et al. 1996).

	Heavy Fuel Oil	Orimulsion 100
O$_2$ (%)	1.0	0.95
CO (ppm as measured)	40	61
NO$_x$ (ppm @ 3% O$_2$)	273	217
SO$_2$ (ppm)	1605	2228
SO$_3$ (ppm)	8.5	13.2
Bacharach smoke number	1-2	2-3
PM (mg/Nm^3)	415	160

or emulsifying agents. The western Canadian bitumen was 83.4% carbon, 10.5% hydrogen, and 5% sulfur, compared to the Orinoco bitumen composition of 85.3% carbon, 9.7% hydrogen, and 4% sulfur noted in the previous chapter. The flame from the Canadian fuel was reported to be bright and

stable, and shorter and more intense than a No. 6 fuel oil flame. The study concluded that the fuel appeared to be "an acceptable alternative to No. 6 fuel oil" (Wong et al. 1989).

Burner Development
Tests of different atomizer designs were conducted in 1988 using Orimulsion (Tombs 1996). These tests evaluated a mechanical pressure jet atomizer and three dual-fluid atomizers in a full-scale burner installed at a pilot-scale test facility. The tests sought to develop a burner-atomizer combination that did not exert excessive shear and that created good mixing of the fuel and atomizing fluid (steam). The dual-fluid atomizers tested were Y-jet, F-jet, and advanced F-jet, with the advanced F-jet design found to be suitable for full-scale operation. Figure 3-2 presents the F-jet and advanced F-jet designs. Different burner configurations were tested using Orimulsion 100 and Orimulsion 400 in the spring of 1998 by DB-Riley for SK Power of Denmark (DB-Riley 1998). The tests also evaluated a number of spray atomizer designs and compared performance of the Orimulsion formulations with the performance of heavy fuel oil. The tests concluded that Orimulsion 400 had similar combustion performance to Orimulsion 100 (Hall 1998).

Trial Tests
Pilot-scale tests were conducted by the Italian Electricity Generating Board (ENEL) at their research and development facility using a 50 MWth full-scale burner in a single burner test rig (De Santis et al. 1996). These tests compared the combustion and emissions characteristics of Orimulsion 100 with a high sulfur (2.8%) No. 6 fuel oil using two burners and several different atomizing nozzles. Measurements of CO, NO_x, SO_x, volatile organic compounds (VOCs) and polycyclic aromatic hydrocarbons (PAHs) were made during the combustion trials. In addition, the conversion of SO_2 to SO_3 was also measured.

SO_2 values ranged from 5750 to 6250 mg/Nm^3 for Orimulsion 100, with SO_3 emissions less than 5 ppm. These SO_2 concentrations correspond to approximately 2200 to 2380 ppm (at 77°F). The SO_3 emissions are lower than those reported in other tests, with the difference attributed to lower levels of vanadium having deposited on the test facility's surfaces than is typical for full-scale systems.

The ENEL tests compared emissions from two types of burners, a three fuel (coal/oil/gas) Babcock & Wilcox XCL low NO_x burner and a dual-fuel (oil/gas) ENEL/Ansaldo TEA Mark 2 low NO_x burner. For the XCL burner, NO_x emissions were approximately 30% lower when burning Orimulsion 100 compared to operation with No. 6 fuel oil. NO_x emissions from the XCL burner ranged from approximately 190 mg/Nm^3 (150 ppm) at 3% O_2 to about 320 mg/Nm^3 (260 ppm) at 4.5% O_2 when burning Orimulsion 100 and from 300 mg/Nm^3 (240 ppm) at 1.8% O_2 to approximately 390 mg/Nm^3 (320 ppm) at 3.8% O_2 when burning No. 6 fuel oil. When using the TEA burner, NO_x emissions from Orimulsion 100 ranged from approximately 350 mg/Nm^3 (280 ppm) at 1.5% O_2 to approximately 570 mg/Nm^3 (460 ppm) at 4% O_2, and from about 250 mg/Nm^3 (200 ppm) at 2% O_2 to about 320 mg/Nm^3 (260 ppm) at 4.5% O_2 when burning No. 6 fuel oil.

The O_2 level at which CO emissions exceeded 100 mg/Nm^3 (87 ppm) when using the XCL burner was approximately 2% when burning No. 6 fuel oil and approximately 3.5% when burning Orimulsion 100. Because it was expected that the CO "knee"* would be at a lower O_2 level for Orimulsion 100 than for No. 6 fuel oil, further investigation was undertaken. It was determined that the Orimulsion was incorrectly heated during these tests, leading to the higher CO levels when burning Orimulsion 100 compared to No. 6 fuel oil. Further tests using several different atomizing nozzle designs found that only one nozzle design could achieve CO emissions lower than 50 ppm at O_2 levels less than 1%, but that atomizer also resulted in the highest NO_x emissions of the four atomizers tested. It was not clear which atomizer of those tested produced the lowest CO and NO_x emissions, but the study concluded that NO_x emissions for Orimulsion 100 would be 15-30% higher than for No. 6 fuel oil. The study also concluded that Orimulsion responded to low NO_x firing techniques in a manner

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*Nearly all combustion systems exhibit a rapid and substantial increase in CO below a certain O_2 level. This point is often termed the "CO knee," and will vary from one unit to another.

Oil Port

Annular Mixing Chamber

il

Atomizing Fluid

Inner Body

Exit Port

Turbulent Recirculating Flow

F-Jet Atomizer

ap Nut

tomizer uter ody

il Passage

Steam Passage

Atomizer Inner Body
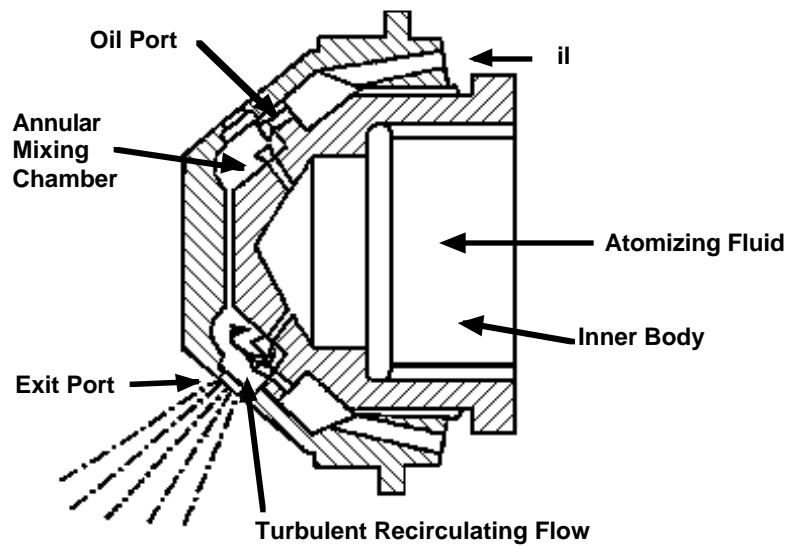
Mixing Chamber
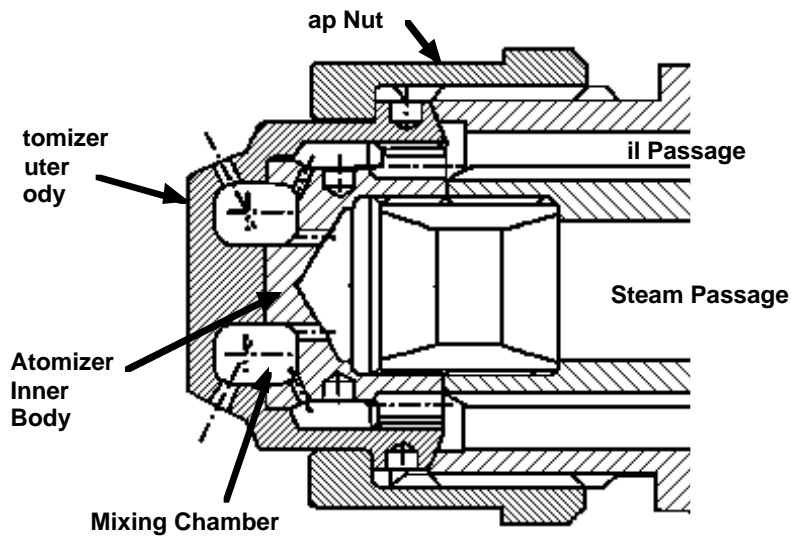
Advanced F-Jet Atomizer

Figure 3-2. F-jet (top) and advanced F-jet atomizers used in Orimulsion combustion tests at PowerGen's Power Technology Centre (Tombs 1996).

similar to No. 6 fuel oil, but that additional atomizer testing was needed to determine the optimal design for the particular burners they were testing.

PM emissions from Orimulsion 100 were measured at between 220 and 260 mg/Nm^3. The particle size distribution (as determined using scanning electron microscope) showed 73.1% of the particle mass being less than 10 μm and 21.2% < 1.0 μm for Orimulsion 100. The PM from Orimulsion 100

combustion had 84% unburned carbon (percent of the ash as measured by SEM-EDX). For No. 6 fuel oil, the distributions showed 87.1% < 10 μm and 51.3% < 1.0 μm, and the unburned carbon value was 78.5% (De Santis et al. 1996). The unburned carbon values for these tests were significantly higher than those reported in other studies, suggesting that site-specific factors influenced these results.

VOC emissions were measured at 277 μg/Nm^3 when burning Orimulsion 100 and 350 μg/Nm^3 when using No. 6 fuel oil. PAH emissions were measured at 7.9 μg/Nm^3 when using Orimulsion 100, compared to 5.2 μg/Nm^3 when using No. 6 fuel oil (De Santis et al. 1996).

Reburning Development

Bertacchi et al. (1997) conducted tests of Orimulsion 100 as a reburn fuel** in a 6 MWth pilot-scale test facility. These tests showed baseline NO_x emissions when using Orimulsion 100 as a reburn fuel were approximately 50 mg/Nm^3 (40 ppm) lower than for a heavy fuel oil under similar conditions. These tests concluded that Orimulsion performed better than heavy fuel oil as a reburn fuel, but that the behavior of Orimulsion was somewhat different than heavy fuel oil. While the NO_x emissions tended to decrease with increasing levels of reburn fuel for heavy fuel oil, increasing the level of reburn fuel with Orimulsion resulted in a decrease followed by an increase in NO_x emissions. Thus, at higher reburn zone stoichiometries, NO_x emissions using Orimulsion as the reburn fuel were higher than those at the same reburn zone stoichiometries, but at lower reburn zone stoichiometries, using Orimulsion 100 as the reburn fuel resulted in lower NO_x emission than using heavy fuel oil as the reburn fuel. The optimum reburn condition using Orimulsion 100 on this pilot-scale unit was about 15% reburn fuel*** in a reburn zone stoichiometry of approximately 0.85, which resulted in NO_x emissions of 240-250 mg/Nm^3 (195-205 ppm), compared to baseline emissions of 600 mg/Nm^3 (490 ppm).

Additional testing was conducted in a 1 MW combustion test facility by Irons and Jones (1996), who also concluded that Orimulsion 100 had properties that would make it suitable for use as a reburn fuel.

Air Pollution Control Equipment Evaluation

During full-scale demonstration of Orimulsion 100 operation at Florida Power & Light's Sanford Plant in 1991, two pilot-scale baghouses were evaluated for their effectiveness in controlling PM from Orimulsion combustion (Olen et al. 1991). A 5,000 acfm pulse jet cleaned baghouse and a 10,000 acfm reverse gas cleaned baghouse were tested. The pulse jet unit had 48 bags, and a range of fabric materials were tested on this unit, including Huyglas, Tefaire, P84, and Ryton/Rastex. The larger reverse gas cleaning unit used 80 bags of Gore-Tex membrane laminated to a fiberglass fabric supplied by W.L. Gore and Associates, Inc. The larger unit had an air to cloth ratio of 3.8 at a maximum gas flow rate of 14,000 acfm.

The study concluded that a pulse jet baghouse can be used to control PM emissions from the combustion of Orimulsion. However, several conditions apply to the successful application of this technology. The bags required coating with a sorbent material prior to startup to protect the bags from the high SO_3 levels typical of Orimulsion 100 emissions. In addition, it was determined that maintaining a low acid dewpoint through high baghouse inlet temperature and low excess O_2 (typical high load conditions) was necessary to ensure adequate bag life. The tests also concluded that prolonged operation would not be feasible at high acid dewpoint conditions such as those that would be present during low load operation, unless adequate sorbent material was co-injected into the flue

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**Reburning is a method of NO_x control that injects a fraction of the fuel heat input at a point downstream of the main burners to create a fuel-rich zone in the furnace, followed by injection of burnout air to allow complete burnout of the hydrocarbons. Reburning can achieve NO_x emissions reductions of 40-60% (Meadows et al. 1996).

***15% of the total heat input to the boiler is injected into the reburn zone.

gases to protect the bags from degradation from SO_3.

Testing of the reverse gas cleaned baghouse was not able to determine whether such a design would be appropriate for use in Orimulsion applications. While evaluation of the filter media indicated normal wear patterns (compared to other fossil fuel applications), the tests were discontinued before adequate data could be gathered to determine effectiveness of additives or long-term operation (Olen et al. 1991).

Full-Scale Testing and Operation
Plants Currently Operating
A number of boilers are currently using Orimulsion as their primary fuel (in most cases the sole fuel) in commercial operations. Table 3-2 lists those plants that were commercially operating or have commercially operated using Orimulsion as of November 1999. In addition to these plants, Orimulsion is also being used at a 770 MWe coal-fired power plant in Germany as fuel for the plant's auxiliary boilers. The Ibbenbüren plant will use up to 22,000 tons of Orimulsion annually for startup and fuel support when coal volatile content drops below a given point (Bitor Europe 1998).

Table 3-2. Plants that have operated or are were operating commercially as of December 2000 using Orimulsion (Olen 1998b, Quig and Woodworth 1997, Quig 1999, Garcia 1999, Miles 1999, Garcia 2000).

Country	Plant Name	Operation Date[1]	Original Fuel Design	Boiler Design	Plant/Unit Rating (MW)	Orimulsion Consumption, tons/yr
Canada	NB Power Dalhousie #1	1994	Heavy fuel oil	T-fired	105	700,000[2]
	NB Power Dalhousie #2	1994	Pulverized coal	T-fired	215	
Denmark	SK Power Asnaes #5	1995	Pulverized coal	Opposed wall-fired	640	1,400,000
Italy	ENEL Brindisi Sud #1	1997	Pulverized coal Heavy fuel oil	Opposed wall-fired	660	1,500,000
	ENEL Brindisi Sud #2	1999	Orimulsion	Opposed wall-fired	660	1,500,000
	ENEL Fiumesanto #3, #4	1999	Pulverized coal Heavy fuel oil	T-Fired	2x320	1,300,000 (total for 2 units)
Japan	Mitsubishi Kasei	1992	Heavy fuel oil	T-fired	70 + steam	300,000
	Kashima-Kita #1	1991	Heavy fuel oil	T-fired	95 + steam	375,000[2]
	Kashima-Kita #2	1994	Heavy fuel oil	T-fired	125 + steam	
	Kansai Osaka #4	1994	Pulverized coal	T-fired	156	200,000
	Hokkaido Electric Shiriuchi	1997	Orimulsion	NA[3]	350	100,000
Lithuania	Lietuvos Energija	1995	Heavy fuel oil	Wall-fired	150+steam	150,000
United Kingdom	PowerGen Ince "B" [4]	1991	Heavy fuel oil	Wall-fired	500	1,300,000
	PowerGen Richborough[5]	1991	Pulverized coal	NA	3x120	300,000

1. Initial commercial operation date using Orimulsion.
2. Combined consumption, Units 1 and 2.
3. Information not available.
4. Retired, May 1997.
5. Retired, 1996.

New Brunswick Power Dalhousie Generating Station

New Brunswick Power Corporation's Dalhousie Generating Station has been in operation using Orimulsion since the fall of 1994 (Mulholland 1996). The Dalhousie plant, shown in Figure 3-3, is located in Dalhousie, New Brunswick, Canada, and has two units. Unit 1 is a tangentially-fired unit, rated at 103 MWe, and originally designed to burn a 2.6% S No. 6 fuel oil when it began commercial operation in 1967. The unit was designed by Combustion Engineering (CE) as a three-level, 12-burner unit (New Brunswick Power 1989). Unit 2 was originally designed to burn an indigenous New Brunswick coal with sulfur content of 8%, and is rated at 212 MWe. Unit 2 began commercial operation in 1978 (Kennedy and Sainz 1992). Conversion of the plant to burn Orimulsion began in 1991, following an 18-month demonstration of Orimulsion operation on Unit 1.

Dalhousie Demonstration Tests

A comprehensive report of the 1988 Orimulsion demonstration program at Dalhousie was summarized in a report on the demonstration prepared by NB Power (New Brunswick Power 1989).At the time the report was written, the Dalhousie Station had approximately 2,500 hours of equivalent full load operation, with plans for a further 1,700 hours of equivalent full load operation. Measurements of fuel handling characteristics, boiler thermal efficiency, carbon in ash, ESP performance, and pollutant emissions were made during the demonstration. The results of those tests are summarized below and in Table 3-3.

Figure 3-3. Photograph of Dalhousie Generating Station, Dalhousie, New Brunswick, Canada.

Unit 1 burners used CE internal mix atomizers with steam as the atomizing fluid. The burners were originally designed for mechanical atomization, but were retrofit for steam atomization for the Orimulsion tests. The nozzle fuel ports were increased in size to provide an increased flow capacity of approximately 20% over that used during No. 6 fuel oil operation. The unit was able to achieve 98 MWe using all 12 burners when using Orimulsion, compared to a maximum load of 104 MWe when using No. 6 fuel oil.

During testing, the boiler thermal efficiency dropped from 87.2% using No. 6 fuel oil to 82.6% using Orimulsion 100. The reduction in efficiency was due to the effect of the high water content of Orimulsion 100 as well as the increase in boiler tube fouling associated with Orimulsion 100 compared to the No. 6 fuel oil. Carbon in ESP ash levels were consistently very low (near 1%), while those for the No. 6 fuel oil ranged from over 45% at 0.7% excess O_2 to 35% at 2.5% excess O_2.

The ESP was in operation during all tests. At less than 50% load, the ESP collection efficiency was greater than 95%, but dropped to approximately 86% at full load. This drop in efficiency was attributed to an increase in the flue gas volume (and higher particle velocities) due to higher ESP inlet temperatures (450 °F during the demonstration compared to approximately 340 °F when using No. 6 fuel oil). A further contributing factor was believed to be the lower ash density when using Orimulsion 100 compared to No. 6 fuel oil. The report concluded that the ESP could effectively collect Orimulsion ash at higher efficiencies if the flue gas mass flow, temperature, ash density, particle resistivity, and particle size were properly taken into account.

PM loading at the economizer exit was approximately 250 mg/m3 at 70 °F and 0.5% O_2 (at the economizer exit) when using Orimulsion 100 compared to an estimated 105 mg/m3 at 70 °F and 0.8% O_2 for No. 6 fuel oil, again at the economizer exit.

The particle size distribution of Orimulsion ash was considerably smaller than that of ash from No. 6 fuel oil. PM generated by the combustion of Orimulsion 100 during the Dalhousie demonstration was found to be 98% by weight (wt%) less than 10 μm in diameter and 50 wt% less than 0.3 μm in diameter, as seen in Figure 3-4. This compares to approximately 75 wt% less than 10 μm in diameter and 35 wt% less than 0.3 μm in diameter for PM from No. 6 fuel oil. This resulted in an ash of much lower density (5-10 lb/ft3 for Orimulsion 100 compared to 25 lb/ft3 for No. 6 fuel oil). The ash from Orimulsion 100 combustion consisted of 16% S, 11% V, 2% C, and 1% Fe, with the majority (55%) being reported as "Other" (oxygen, hydrogen, nitrogen, and trace metals including magnesium). Ash from No. 6 fuel oil combustion consisted of 36% C, 13% V, 6% S, and 1% Fe, with 36% "Other." The Orimulsion 100 ash had substantially less carbon in the ash than did the heavy fuel oil ash over the range of O_2 levels tested. Figure 3-5 shows the carbon in ash measurements for Orimulsion 100 and heavy fuel oil as a function of stack O_2 level.

Table 3-3. Emissions measured during Dalhousie Station Unit 1 Demonstration (New Brunswick Power 1989).

	Orimulsion 100	HFO
CO (at 0.7% O_2)	30 ppm	60 ppm
NO_x (at 3% O_2, 90 MWe)	180-215 ppm	180-190 ppm
PM (at economizer exit)	250 mg/m3 at 70 °F	105 mg/m3 at 70 °F[1]
Particle Size Distribution	98% < 10 μm 50% < 0.3 μm	75% < 10 μm 35% < 0.3 μm
SO_2 (at 3% O_2, uncontrolled)	2270-2350 ppm	1540-1560 ppm
SO_3	2-15 ppm	NA[2]

1. Reported estimated value of PM loading
2. Not available

CO emissions were consistently lower than those from No. 6 fuel oil. At 0.7% O_2, the boiler exit CO level using Orimulsion 100 was measured at approximately 30 ppm, while the boiler exit CO level using No. 6 fuel oil was measured at approximately 60 ppm. CO emissions were influenced by the temperature of the Orimulsion and the atomizing steam and by the differential pressure between the fuel and the steam. At a load of 90 MWe and 0.5% excess O_2, CO emissions were reduced from 20 ppm to less than 10 ppm as the Orimulsion temperature changed from 125 °F to 150 °F. Figure 3-6 shows the variation in CO emissions with changing O_2 levels at different loads and compared to heavy fuel oil. Changing the atomizing steam temperature from 424 °F to 500 °F resulted in a reduction of CO from approximately 50 ppm to approximately 30 ppm. As the differential pressure was changed from +10 psig to +4 psig (steam to fuel), the CO emissions increased from 50 ppm to approximately 95 ppm.

At the time the demonstration was conducted, the Dalhousie Station did not use an FGD system or NO_x controls, so NO_x and SO_x emissions in this report reflect uncontrolled emissions. Uncontrolled SO_2 emissions when using Orimulsion ranged from 2270 to 2350 ppm at 3% O_2, compared to 1540 to 1560 ppm at 3% O_2 for No. 6 fuel oil. NO_x emissions at 90 MWe load ranged from 180 to 215 ppm when firing Orimulsion compared to 180 to 190 ppm when firing No. 6 fuel oil.

SO_3 emissions from the combustion of Orimulsion were measured at between 2 and 15 ppm during optimized operation, with the lower value being measured under clean boiler conditions and the higher value measured after the boiler internal surfaces had been fouled due to continuous operation with Orimulsion. SO_3 emissions as high as 35 ppm were noted during initial test runs, but as operators became more familiar with Orimulsion operation and were able to reduce the excess O_2 levels, SO_3 emissions were consistently in the lower range (New Brunswick Power 1989). Figures 3-7 and 3-8 show the relationship of SO_3 emissions to acid dewpoint temperature and the variation of daily acid dewpoint temperature in the stack over the demonstration test period, respectively.
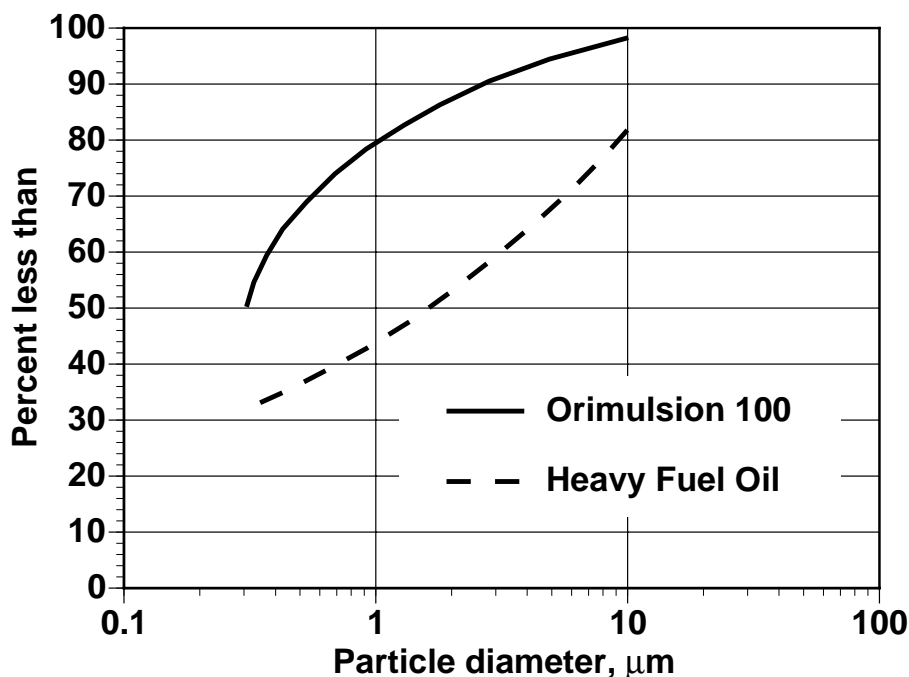
Figure 3-4. Particle size distribution for PM emitted from the combustion of heavy fuel oil and Orimulsion 100 during demonstration testing at NB Power Dalhousie Generating Station (New Brunswick Power 1989).
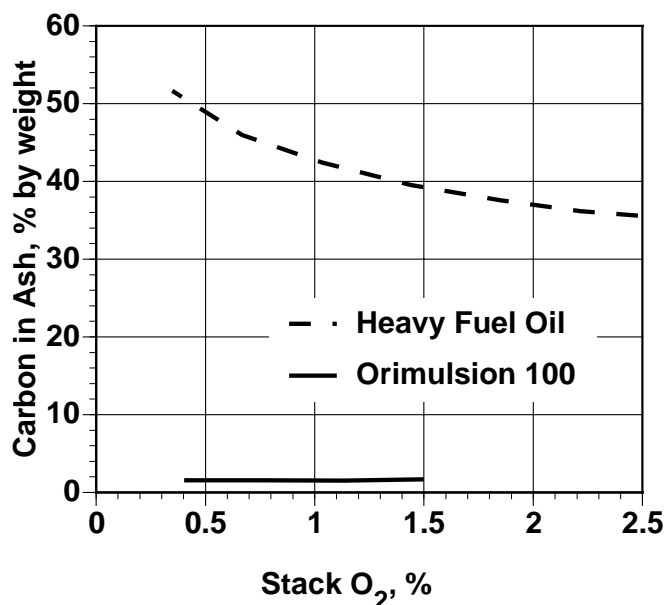
Figure 3-5. Carbon in ash in PM emitted from the combustion of heavy fuel oil and Orimulsion 100 during demonstration testing at NB Power Dalhousie Generating Station (New Brunswick Power 1989).

Boiler efficiency was measured at 82.4% during Orimulsion 100 firing and 87.4% during HFO firing. The unit's net heat rate was determined to be 10,972 Btu/kW-hr when using Orimulsion 100 and 9,743 Btu/kW-hr when using HFO (Hidalgo et al. 1989).

Conversion to Permanent Orimulsion Operation
Conversion of the Dalhousie plant to permanent Orimulsion operation was completed in 1994. As part of the conversion, the plant installed new fuel transfer, handling, and storage facilities, new burner tips for Unit 2 (the No. 6 oil burners in Unit 1 were not changed), a new common flue gas desulfurization (FGD) system, and a new common wastewater treatment facility (Kennedy and Sainz 1992). The FGD system was designed to reduce SO_2 emissions by 90% compared to the preconversion levels. The FGD system is a wet limestone system, using a single absorption tray and five spray headers in a counter-current design. The system was designed to produce wallboard grade gypsum with a minimum of 92% $CaSO_4 \cdot 2H_2O$ at a Ca to S stoichiometric ratio of 1.03 (Kennedy and Sainz 1992).

During commercial operation with Orimulsion 100, CO emissions were reported to be 30 ppm or less, at boiler O_2 levels of less than 1%. NO_x emissions were measured at 290 ppm (corrected to 3% O_2) during the same test program. These NO_x values compare to the roughly 200 ppm measured during demonstration testing. SO_2 emissions were measured at just under 200 ppm (corrected to 3% O_2) in the stack. This compares to the uncontrolled concentrations of 2300 ppm measured during the demonstration testing, giving a reduction of approximately 91% (Janati 1997). PM emission rates when using Orimulsion 100 over long-term operation have been reported as being consistently around 0.015 lb/10[6] Btu (Janati 1997, Irvine and Eagles 1998).

The wastewater treatment plant was designed to reduce the bitumen content of any wastewater from levels as high as 10,000 mg/l to less than 10 mg/l to meet applicable government requirements. In addition, the treatment plant was also designed to remove trace metals such as vanadium. Bench scale testing of the treatment process indicated that vanadium could be reduced from levels as high as 7,000 mg/l to less than 0.5 mg/l to meet the applicable government regulations. Efforts were also made to increase the density of the collected fly ash and pelletize it to allow it to be used as a feedstock for a vanadium recovery process and minimize the landfill requirements of the ash
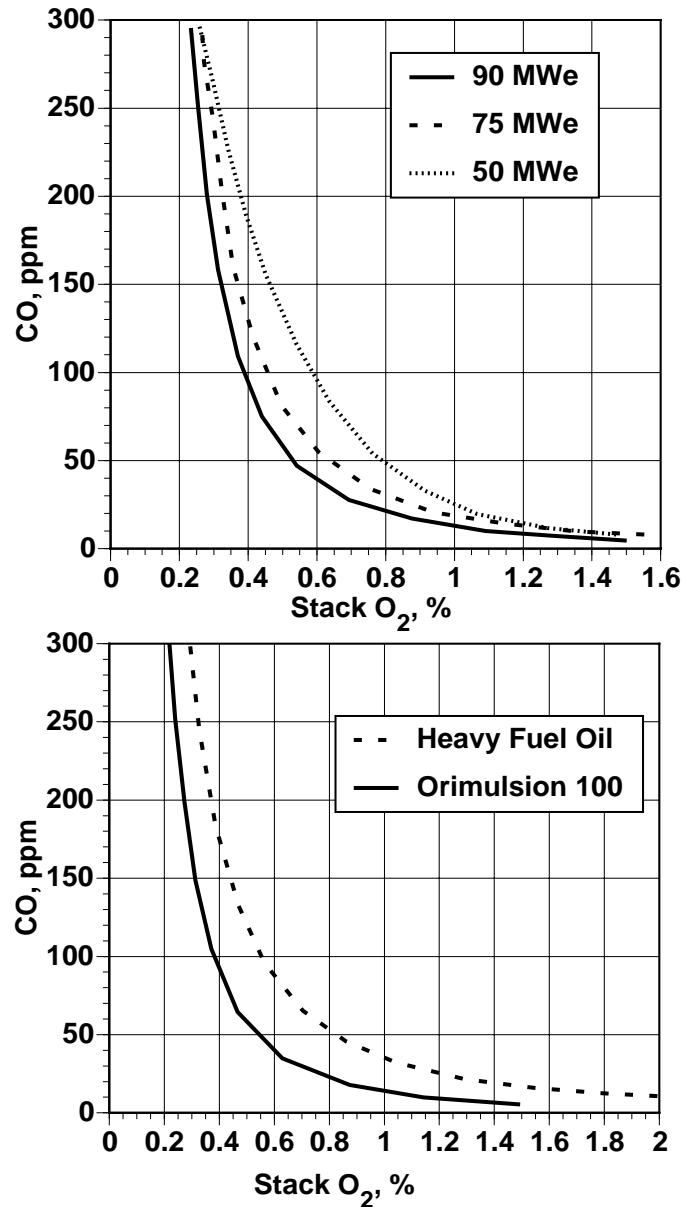
Figure 3-6. CO as a function of stack O_2 levels measured during combustion testing of heavy fuel oil and Orimulsion 100 at the NB Power Dalhousie Generating Station. The top plot shows CO at different loads when burning Orimulsion 100 and the bottom figures compares CO emissions from heavy fuel oil and Orimulsion 100 at 90% load (New Brunswick Power 1989).

(Kennedy and Sainz 1992). The collected fly ash was quite low in density compared to fly ash from heavy fuel oil or coal, resulting in mechanical problems in maintaining flow of the ash in the ESP hoppers. These problems were solved by lining the ESP hoppers with stainless steel, removing surface irregularities in the ash flow path, and wetting the ash after removal from the hopper to stabilize it and increase the density. As of late 1998, the collected fly ash was being prepared and sold for vanadium recovery (Irvine and Eagles 1998).

Use of Orimulsion 400
The Dalhousie plant converted from the original formulation (Orimulsion 100) to Orimulsion 400 in

September 1998. The formulation of Orimulsion 400 that was being used had significantly lower viscosity than the original formulation of Orimulsion, resulting in some operational changes to achieve optimum fuel pressure at the burners and to the burner tip port sizes. During the initial six weeks of operation with Orimulsion 400, the plant noted lower emissions of CO and NO_x and less unburned carbon than was measured with Orimulsion. CO emissions were reported as near zero with stack O_2 at 0.5%, and NO_x emissions had dropped from 125 ng/J to 105-110 ng/J (Irvine and Eagles 1998).

Plans have been made to install a wet ESP on the common stack at Dalhousie to reduce the level of
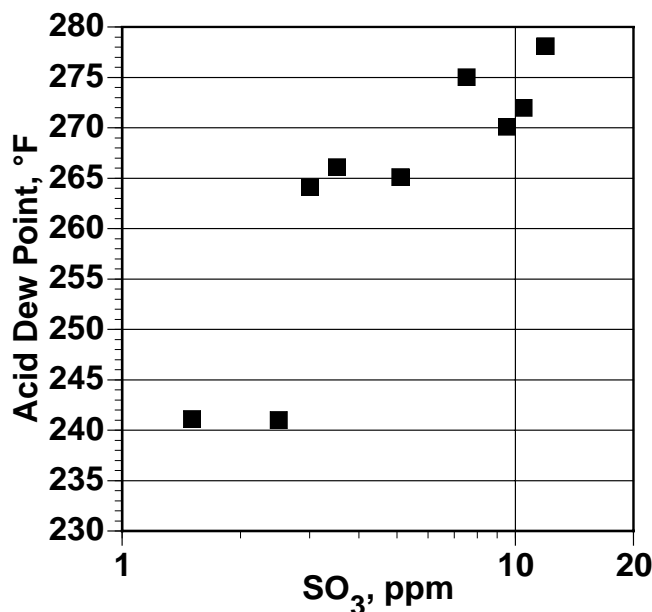
Figure 3-7. Relationship between the acid dewpoint and SO_3 emissions measured during Orimulsion 100 demonstration testing at the NB Power Dalhousie Station (New Brunswick Power 1989).
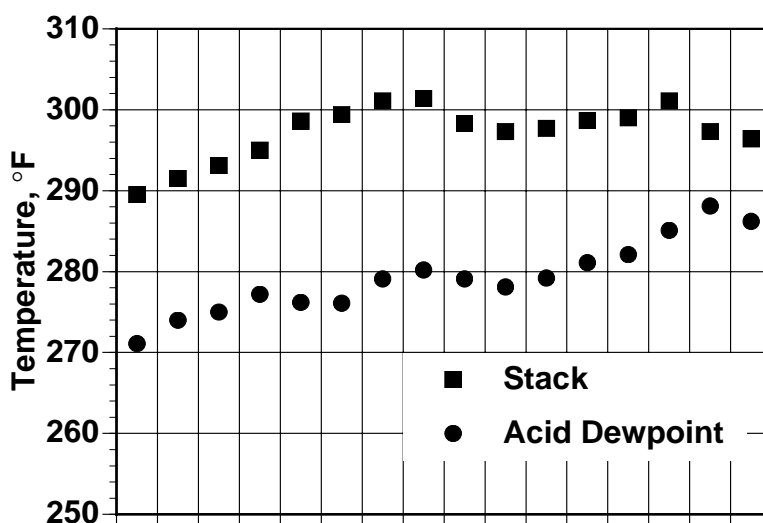
Figure 3-8. Relationship between stack and acid dewpoint temperature for each day during Orimulsion 100 demonstration testing at NB Power Dalhousie Station (New Brunswick Power 1989).

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SO_3 emissions and eliminate any visible plume, even though there is no regulatory requirement for installing the system (Irvine and Eagles 1998). This approach may be necessary in cases where other means of SO_3 reduction have not been successful.

Kansai Electric Power Company Osaka No. 4
The Osaka No. 4 boiler of Japan's Kansai Electric Power Company (Kansai) was converted to operate using Orimulsion in 1994, and results of emission and performance testing were reported in 1996 (Kaneko et al. 1996). The 156 MWe boiler was originally designed for coal and oil firing in 1960, and has burned only oil since 1970.

Reported CO emissions from both Orimulsion 100 and heavy fuel oil (HFO) were consistently less than 100 ppm for O_2 levels ranging from 0.6 to 3.0%. CO emissions from Orimulsion 100 appeared to be slightly higher than for HFO at O_2 levels less than 1%, but were otherwise nearly the same for both fuels.

NO_x emissions ranged from approximately 120 ppm at 0.6% O_2 to approximately 200 ppm at 3% O_2 when using Orimulsion 100 and from approximately 80 ppm at 0.8% excess O_2 to approximately 120 ppm at 3% O_2 when firing HFO (all values corrected to 4% O_2). Uncontrolled SO_2 concentrations from Orimulsion 100 combustion were reported as approximately 2500 ppm, corrected to 1% O_2. CO, NO_x, and SO_2 concentrations for Orimulsion 100, heavy fuel oil, and nonemulsified Orinoco bitumen during testing at Osaka No. 4 are shown in Figure 3-9.

PM emissions and unburned carbon in the ash at the Osaka No. 4 boiler measured during operation with Orimulsion 100, heavy fuel oil, and Orinoco bitumen showed that emissions decreased as stack O_2 levels increased. PM emissions were slightly higher and unburned carbon levels were approximately the same when using Orimulsion compared to firing with heavy fuel oil. Unburned carbon levels were measured as slightly higher for heavy fuel oil than for Orimulsion 100 at O_2 levels less than about 1%, and slightly lower than for Orimulsion for higher O_2 levels. Reported SO_3 emissions increased as O_2 level increased for both Orimulsion 100 and heavy fuel oil, with emissions during Orimulsion firing being consistently higher than those measured during heavy fuel oil firing. Figure 3-10 shows emissions of PM, unburned carbon, and SO_3 from Orimulsion 100, heavy fuel oil, and Orinoco bitumen at the Osaka No. 4 plant.

Kashima-Kita Electric Power Company
The Kashima-Kita Electric Power Company of Japan is also using Orimulsion for electric power generation. Olen and Alcantara (1993) noted that the plant made extensive modifications to the ESP to handle the ash generated by the combustion of Orimulsion. A third field was added to the existing ESP to handle the greater ESP particle loading. Part of the increased particle loading was due to the injection ammonia for conversion of SO_3 to particulate ammonium sulfate. This approach has also been applied to the Osaka No. 4 boiler. Long spiked discharge electrodes are also used in the Kashima-Kita ESP to overcome current suppression due to space charge effects. These modifications have resulted in PM emissions of less than 0.013 lb/10[6] Btu or 20 mg/Nm[3] at full load, with an inlet loading of 550-650 mg/Nm[3]. This inlet loading compares with roughly 280 mg/Nm[3] without ammonia injection (Olen and Alcantara 1993).

SK Energy Asnaes Unit 5
Orimulsion is also being used in Denmark by SK Energy at the Asnaes Generating Station, Unit 5. Unit 5 is a 700 MW opposed wall fired unit originally designed to burn coal (Quig and Woodworth 1997).

Orimulsion 100 Use at Asnaes
Emissions testing was conducted when firing Orimulsion 100 in this unit in 1995 (SK Energy undated). Measurements of CO, CO_2, NO_x, O_2, and SO_2 were taken using CEMs, and extractive samples of SO_3, trace elements, and PM were also taken. In addition, measurements of trace elements in the plant wastewater and scrubber sludge were made. CO measurements for these tests were not reported in the literature. NO_x emissions were reported to be 150-180 ppm, or 30-40% lower than
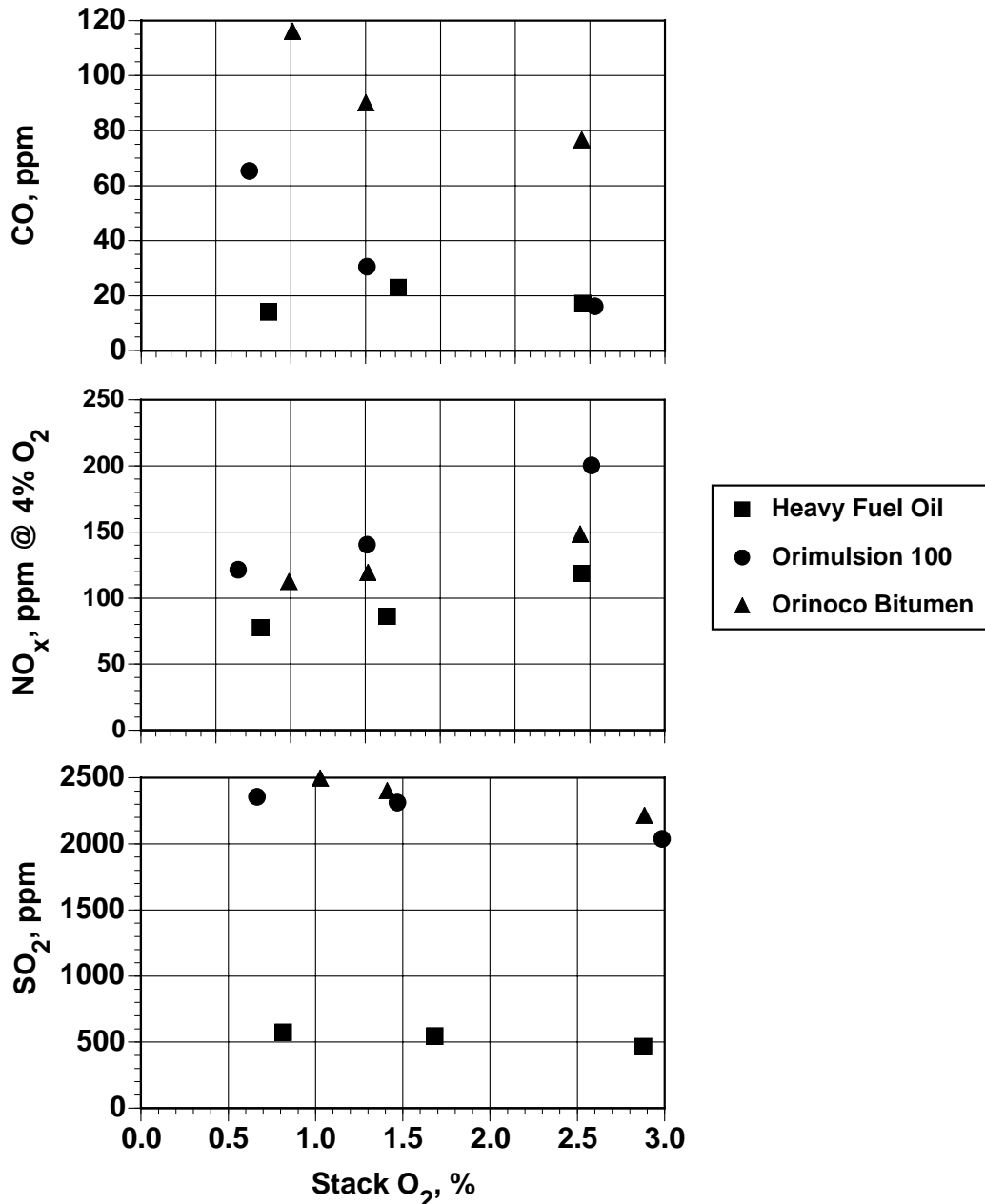
Figure 3-9. CO, NO$_x$, and SO$_2$ emissions at Kansai Electric Company Osaka No. 4 plant (Kaneko et al. 1996).

those measured during operation using coal at the same plant. SO$_2$ emissions were measured at 315 mg/Nm^3, and SO$_3$ emissions at 7.2 mg/Nm^3. Across the heat exchanger (air preheater), SO$_2$ concentrations dropped from 7,228 to 6,672 mg/Nm^3, with the FGD system reducing SO$_2$ concentrations by 95%. SO$_3$ emissions dropped from 301 mg/Nm^3 upstream of the heat exchanger to 16.6 mg/Nm^3 downstream, with the scrubber reducing SO$_3$ concentration by less than 57%. PM emissions were measured at 12.1 mg/Nm^3, with a mass emission rate of 16.6 kg/hr. O$_2$ levels were measured at 5.6% during these tests (SK Energy undated).

The tests conducted at Asnaes also measured particle size distributions using a cascade impactor. Less than 1% of the total particle mass captured during these tests was larger than 1.3 µm in diameter,

and 75% were smaller than 0.35 μm. These measurements are shown in Figure 3-11.

Measurements of trace metal concentrations in the flue gas, the captured fly ash, in wastewater, and in scrubber sludge were also made during the tests at Asnaes. These effluent streams were analyzed for concentrations of Al, As, Cd, Cr, Cu, Ca, Hg, Mn, Mg, Ni, Pb, Se, V, and Zn. Concentrations of these metals in the stack gas are presented in Table 3-4. The reported stack emission concentrations are somewhat surprising, since both Ni and V concentrations are reported as below detection limits, while measurable quantities of Mg and Se are reported with relatively high levels of Se in both the solid and gas phase fractions. These results are in contrast to the reported trace element concentrations in the fly ash, shown in Table 3-5. The fly ash Ni and V concentrations are very high, at 14,000 mg/kg for Ni and 59,000 mg/kg for V (measured in dry samples). The Mg level is also quite high, as would be expected because of the Mg content of the fuel. The measurement of the Asnaes stack sample and the fly ash suggest that in this case the Ni and V emissions are primarily in the collected fly ash and
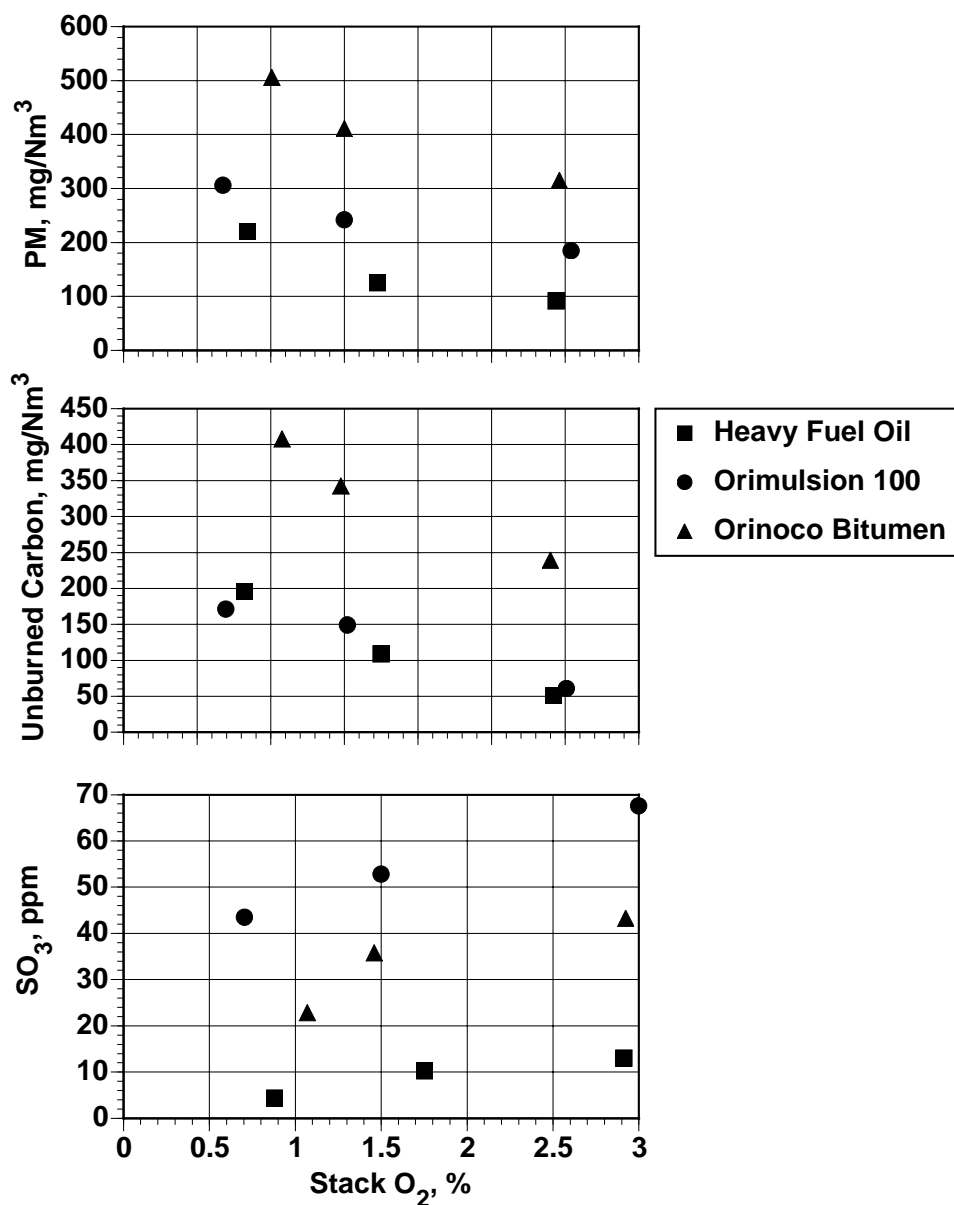
Figure 3-10. Emissions of PM, unburned carbon, and SO$_3$ at Kansai Electric Company Osaka No. 4 plant

3-16
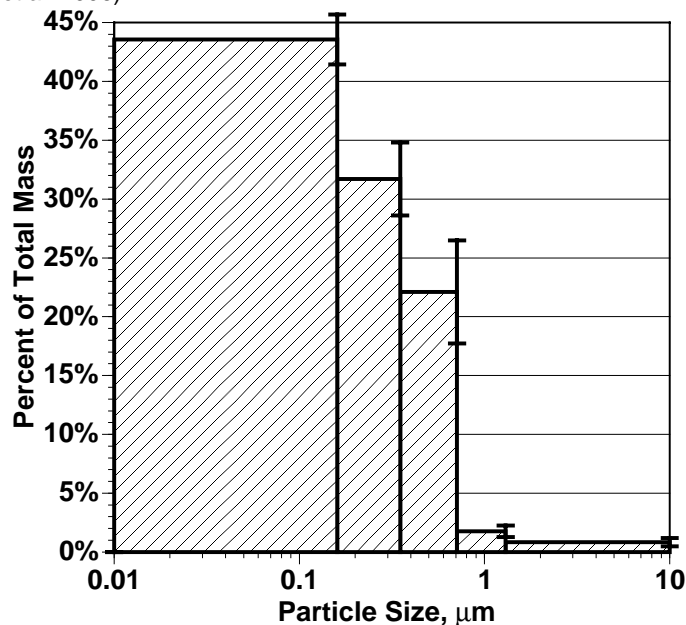
Figure 3-11. Particle size distribution for PM from the combustion of Orimulsion 100 measured at SK Energy Asnaes Unit 5 (SK Energy undated).

Table 3-4. Stack trace metal emissions in mg/Nm^3 measured at Asnaes Unit 5 (SK Energy undated).

	Solid Phase	Gas Phase	Total	No. of non-detects (of 4 solid and 4 gas phase measurements total)
Al	< 0.178	0.0356	< 0.214	4 solid, 0 gas
As	< 0.685	< 0.0356	< 0.721	3 solid, 2 gas
Cd	< 0.0071	< 0.0004	< 0.0075	4 solid, 4 gas
Cr	< 0.0214	< 0.0018	< 0.0231	4 solid, 4 gas
Cu	< 0.0214	< 0.0018	< 0.0231	4 solid, 4 gas
Ca	0.0294	< 0.0535	0.0294[1]	0 solid, 2 gas
Hg	< 0.443	2.00	< 2.45	4 solid, 0 gas
Mn	< 0.0178	0.0047	< 0.0225	4 solid, 0 gas
Mg	< 0.0045	0.0445	< 0.0491	1 solid, 0 gas
Ni	< 0.0712	< 0.0035	< 0.0747	4 solid, 4 gas
Pb	< 0.0712	< 0.0035	< 0.0747	4 solid, 4 gas
Se	1.30	4.71	6.01	0 solid, 0 gas
V	< 0.712	< 0.0356	< 0.747	4 solid, 4 gas
Zn	0.0116	< 0.0039	< 0.0155	0 solid, 1 gas

1. The "Total" value may not add up to the sum of the "Solid Phase" and "Gas Phase" values due to non-detects in individual runs.

not in the emitted flue gas or PM.

Tests were also conducted to determine the levels of trace metals in the scrubber sludge. Measurements were taken during operation using coal and Orimulsion to allow an evaluation of the differences in trace elements in the sludge when using the two fuels. Table 3-6 presents the concentrations of the 14 metals listed above plus iron (Fe) measured in the scrubber sludge. As would be expected, the concentrations of Mg, Ni, and V are significantly higher during Orimulsion 100 operation compared with coal, while slightly higher levels of Hg and Se were found in the samples taken during operation with coal. The Cd concentration was also somewhat higher in the Orimulsion sludge sample than in the coal sludge sample, although it is not clear why this difference occurred.

Orimulsion 400 Use at Asnaes
Additional testing was conducted in spring 1999 at Asnaes Unit 5 following conversion of the plant to Orimulsion 400 (Gibb 1999). NO, O_2, SO_3, and trace element concentrations were measured, as were particle size distributions. NO measurements showed an increase from 100 mg/Nm^3 (80 ppm) at 320 MW load to about 200 mg/Nm^3 (160 ppm) at 620 MW load during Orimulsion 400 firing. O_2 levels were maintained between 2.0 and 2.5% for these tests. SO_3 concentrations were reported at 15-20 ppm at the ESP inlet during full load operation. Reported SO_3 concentrations dropped to 4-7 ppm at the ESP outlet and to about 1 ppm at the stack, indicating substantial levels of reduction by the ESP and the FGD system at Asnaes.

PM concentrations were reported to average 87 mg/Nm^3 at the ESP inlet during Orimulsion 400 firing, although the two measurements reported indicated a substantial variation, at 61 and 114 mg/Nm^3. Measurements at the ESP outlet averaged 2.83 mg/Nm^3, resulting in an ESP efficiency

Table 3-5. Trace metal concentrations in Orimulsion 100 fly ash in mg/kg (unless otherwise noted) measured at Asnaes Unit 5 (SK Energy undated).

	Fly Ash, As-supplied, mg/kg	Fly Ash, Dry, mg/kg	Wastewater, mg/L
Al	0.065%	0.075%	0.1082
As	12	13	0.0025
Cd	0.99	1.1	0.016
Cr	42	49	0.0066
Cu	12	14	0.0042
Ca	NM[1]	NM	NM
Hg	1.1	1.3	0.0004
Mn	0.011%	0.013%	0.87
Mg	11%	13%	NM
Ni	12,000	14,000	0.055
Pb	9.8	11	0.03
Se	22	26	0.14
V	51,000	59,000	0.812
Zn	44	51	0.018

1. Not measured.

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of 96.7%. Stack emissions were measured slightly higher than ESP emissions, possibly due to mist from the FGD system. Stack PM emissions averaged 3.3 mg/Nm^3 for 3 test runs.

PM size distributions were also measured at the ESP inlet and outlet and at the stack using cascade impactors during Orimulsion 400 firing. Approximately 79% of the PM mass was smaller than 2.5 μm in diameter at the ESP inlet, compared to 41% at the ESP outlet and 87% at the stack. The total mass concentration of particles less than 2.5 μm in diameter averaged 69 mg/Nm^3 at the ESP inlet, 1.16 mg/Nm^3 at the ESP outlet, and 2.87 mg/Nm^3 at the stack. Based on the reported values, the ESP removed 98% of particles less than 2.5 μm in diameter and 91% of the particles larger than 2.5 μm in diameter. Reentrainment of larger particles was hypothesized as one reason for the lower removal efficiency of the ESP for the particles larger than 2.5 μm in diameter (Gibb 1999).

PM composition was also measured at the same three locations during the Orimulsion 400 tests at Asnaes. Gibb (1999) reported percentages of several oxides and SO_3 in the collected PM for each of the test runs. The majority of PM entering the ESP was vanadium pentoxide (V_2O_5), at 47%. SO_3 made up 38.7% of the PM mass at the ESP inlet, and the remainder was composed of nickel oxide (NiO) and oxides of calcium, magnesium, sodium, and Fe. The percentage of SO_3 in the PM increased and that of V_2O_5 decreased as the PM passed through the pollution control system. PM at the stack was 0.7% V_2O_5 and 75.7% SO_3. NiO made up 0.13% of the PM at the stack, with the rest of the PM being composed of the remaining oxides noted above.

ENEL Brindisi Sud Units 1 and 2 and Fiume Santo Plant

Brindisi Sud Units 1 and 2 are 660 MWe wall-fired boilers operated by the Italian utility, ENEL. Brindisi Sud Unit 1 was originally designed to burn coal, and is equipped with low NO_x burners, OFA,

Table 3-6. Trace metal concentrations in dry scrubber sludge samples taken during operation with coal and Orimulsion 100 from Asnaes Unit 5 (SK Energy undated).

	Sludge, coal operation, mg/kg	Sludge, Orimulsion 100 operation, mg/kg
Al	7.7%	7.6%
As	13	14
Cd	91	130
Cr	120	130
Cu	130	130
Ca	15%	11%
Hg	21	10
Mn	1.3%	1.9%
Fe	3.2%	3.7%
Ni	330	1500
Pb	130	110
Se	290	180
V	220	3300
Zn	1300	1500
Mg	3.3%	5.7%

flue gas recirculation, selective catalytic reduction, and a limestone-gypsum absorber FGD system.

Planned modifications made for Orimulsion use included adding new sootblowers and installing an MgO injection system in the economizer to protect boiler surfaces from SO_3 condensation (Bertacchi et al. 1997). The Fiume Santo plant, located in Sardinia, was also converted to Orimulsion in 1999. This plant was converted directly from heavy fuel oil to Orimulsion 400. Measurements of trace metal emissions were made following conversion of the plant to Orimulsion 400, and the results of these measurements are shown in Table 3-7 (ENEL 1999).

Past Operations
Orimulsion has been used at several plants under normal operating conditions either as short-term test programs over a period of a few weeks or as longer-term evaluations lasting as long as several years to examine the performance of plants when using Orimulsion. In each case, Orimulsion 100 was used and no testing was conducted using Orimulsion 400.

Florida Power & Light Company Sanford Plant
A short-term demonstration test of operation using Orimulsion 100 was conducted at the Florida Power & Light (FPL) Sanford Plant in 1991. The tests were conducted primarily to evaluate the combustion characteristics and potential pollutant emissions when using Orimulsion. During the tests, multi-cyclone PM controls were used, and were determined to be ineffective in removing the small PM generated from Orimulsion 100 combustion (Olen and Alcantara 1993).

The tests took place over a 10 day period, with CEM and extractive samples taken during steady state operation and during operation with sootblowing. The test results were well documented, including reporting of quality assurance and quality control measurements, in a report describing the results (Entropy 1991). NO_x emission rates measured during these tests ranged from 0.463 to 0.576 lb/10^6 Btu when using Orimulsion 100, with the emission rate increasing with load as shown in Figure 3-12. SO_2 emission rates remained relatively constant between 4.15 and 4.23 lb/10^6 Btu, with no significant variation due to load or sootblowing. PM emission rates for individual tests ranged between 0.128 and 0.215 lb/10^6 Btu and did not change appreciably with load. As would be expected, PM emission rates did indicate an increase during sootblowing operation, as seen in Figure 3-13 (Entropy 1991). Note that fewer tests were conducted both at high (90-100%) load and during sootblowing operation than were conducted at medium (50-90%) load, resulting in less certainty with respect to the

Table 3-7. Emissions of trace metal compounds during tests of Orimulsion 400 at ENEL Fiume Santo Plant (ENEL 1999).

Element	Concentration, µg/Nm³	Element	Concentration, µg/Nm³
As	2.7	Pb	5.5
Be	0.1	Pd	2.9
Cd	0.2	Pt	1.4
Co	0.6	Rh	1.0
Cr (III)	7.7	Sb	0.1
Cr (VI)	7.7	Se	6.1
Cr (total)	15.4	Sn	0.8
Cu	6.8	Te	0.1
Hg	0.9	Ti	1.2
Mn	7.3	V	7.2
Ni (total)	14.1		
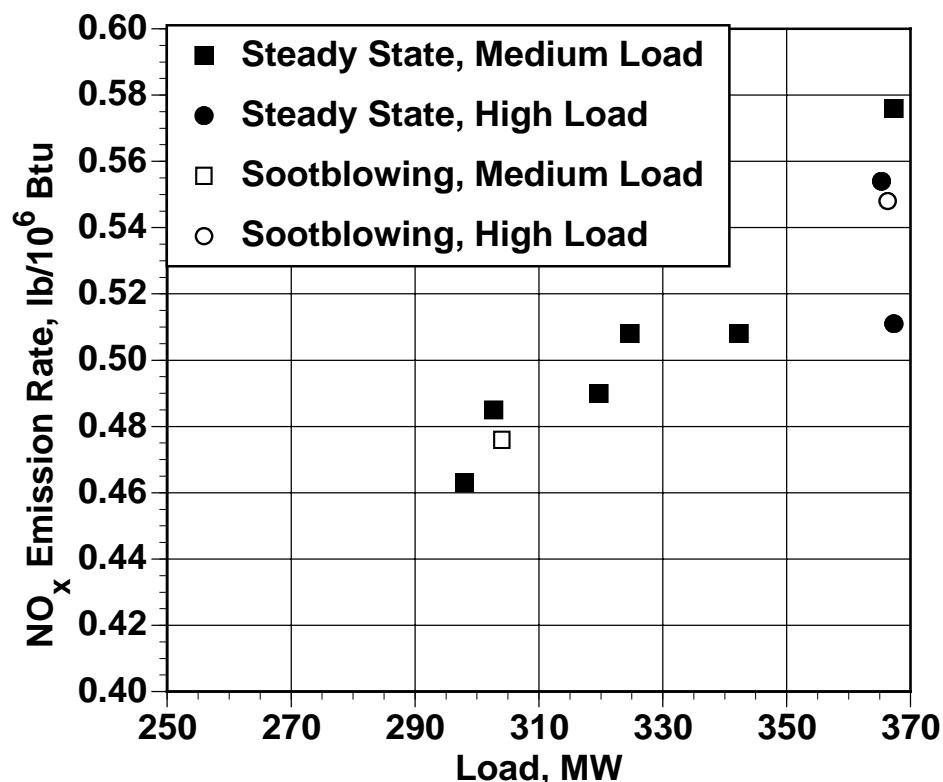
Figure 3-12. NO_x emission rates as a function of load measured during testing of Orimulsion 100 at the Florida Power & Light Sanford Plant (Entropy 1991).

measurements taken at high load and during sootblowing than those taken during steady state, medium load conditions.

The reported PM emission rates at the Sanford plant were similar to the ESP inlet (uncontrolled) levels reported during the Dalhousie Orimulsion demonstration tests. NO_x emissions were reported as being essentially the same as those from the combustion of heavy fuel oil in the same plant under similar conditions of excess air and air preheat levels. The heavy fuel oil was mechanically atomized and the Orimulsion was steam atomized during these tests (Olen and Alcantara 1993).

In addition to measurements of NO_x, SO_2, and PM, measurements of total hydrocarbons (THCs), metals, and sulfuric acid mist (including SO_3) were also taken during the Orimulsion 100 tests (CO was not measured). THC emissions were less than 7 ppm for all but one of the conditions tested, with an average of 5.2 ppm. The single condition exceeding 7 ppm found THC stack concentrations of 15.9 ppm. One set of metals emission rate measurements were taken during steady state operation at high load. Three measurements were taken during a single test day under similar conditions. Metals measured were antimony, arsenic, barium, beryllium, cadmium, chromium, copper, lead, manganese, mercury, Ni, phosphorus, selenium, silver, thallium, V, and zinc. Emission rates of all metals except for Ni and V were less than 36 $lb/10^{12}$ Btu, with mercury emission rates measured at 0.21 $lb/10^{12}$ Btu. Ni emission rates averaged 3,650 $lb/10^{12}$ Btu and V emission rates averaged 14,500 $lb/10^{12}$ Btu. In each case, the PM control device in use was a multiclone. Sulfuric acid mist emission rates were also measured during a single test day, with an average emission rate of 0.00719 $lb/10^6$ Btu being reported (Entropy 1991).

PowerGen Ince and Richborough
Two plants, both operated by PowerGen plc in the United Kingdom, have operated using Orimulsion
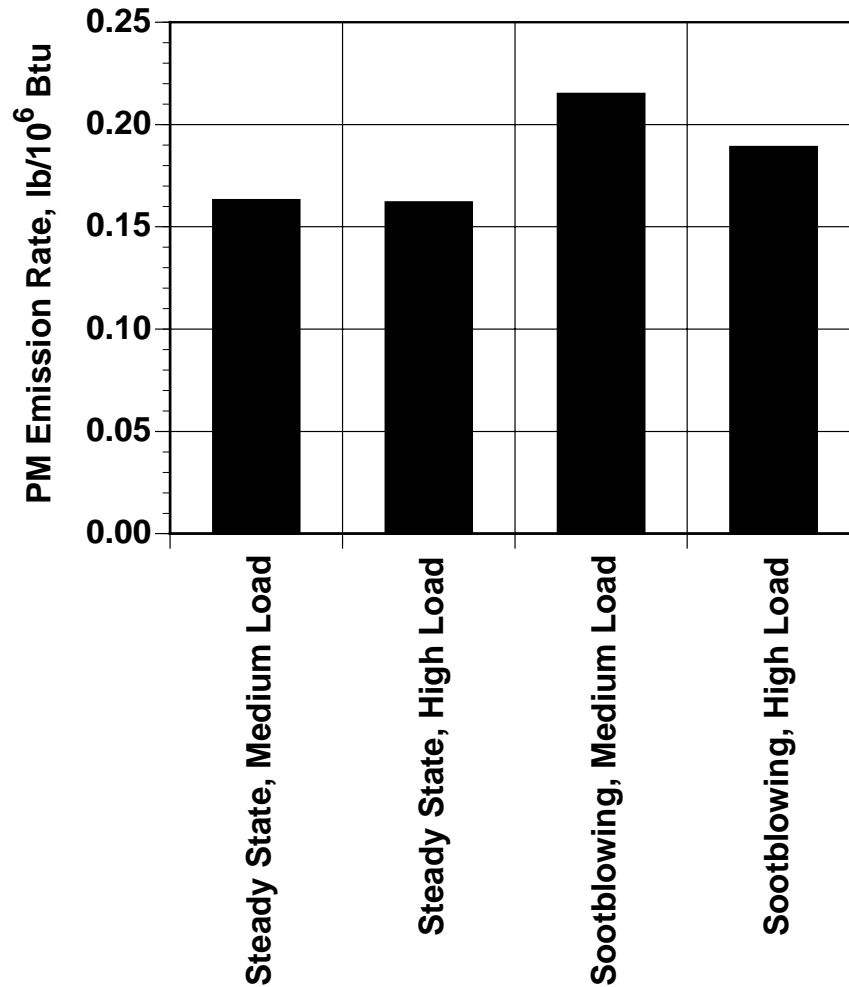
Figure 3-13. Average PM emission rates as a function of test condition measured during testing of Orimulsion 100 at the Florida Power & Light Sanford Plant (Entropy 1991). PM control was multi-cyclone for these tests.

100 as their primary fuel, but are no longer using the fuel. Their experience with the fuel and the emissions associated with its use remain relevant, however. Ince Generating Station is a 2-unit plant, each unit rated at 500 MWe, originally designed to use fuel oil. Ince used approximately 4.8×10^6 tons of Orimulsion between 1991 and the end of 1995, with an average load factor of 70% and availability of 94% during that period. Richborough Generating Station is a 3-unit plant, with each unit rated at 120 MWe, originally designed to burn coal, but later converted to burn oil. The Richborough plant began commercial operation using Orimulsion in 1991, and used approximately 1.65×10^6 tons of Orimulsion 100 between 1991 and the end of 1995 (Tombs 1996).

Initial operation with Orimulsion at Ince required the use of a propane support burner due to excessive shearing and subsequent breakdown of the fuel. Development and application of new atomizers for use with Orimulsion and other liquid fuels resulted in stable combustion, allowing for the use of Orimulsion without need for support fuel. These tests were among the first to use Orimulsion, and subsequent reports of operations at other facilities have not indicated any need for auxiliary fuel during normal operation.

The Ince unit was operated at very low O_2 levels, below 0.1% excess O_2, with negligible carbon-in-ash

($< 0.5\%$). Operation at such low O_2 levels resulted in high CO emissions, on the order of 1000 ppm, which was allowable in the U.K. during the period of Orimulsion use at the plants. The low O_2 level was desired to minimize formation and emissions of SO_3. PM emissions at Ince were typically 30 mg/m^3 or less, with approximately 3,300 tons/yr (3,000 tonnes/yr) of low density ash collected. The ash had a median diameter of less than 1 μm and a resistivity of 10^{10} to 10^{11} ohm-cm, which is within the range in which collection by ESP is feasible. As is currently being done at the Dalhousie plant, the ash generated at Ince was mixed with water to increase the density and to improve the handling characteristics. PowerGen also evaluated the potential for recovering the V present in the ash through a process that was tested in Germany (Tombs 1996). The ESP at Ince was specifically designed to collect the fly ash generated by Orimulsion combustion. The ESP was designed to reduce full load PM emissions from about 350 mg/Nm^3 to approximately 35 mg/Nm^3, a 90% reduction (Olen and Alcantara 1993).

Use of Orimulsion at Ince resulted in a thin deposit of ash building up on the boiler tube surfaces and changes in the boiler temperature distribution. Modifications to the boiler to minimize the impacts of the changed heat transfer characteristics included removal of the radiant superheater originally above the front wall, increasing the number of sootblowers in the convective section from 10 to 32, and converting several of the sootblowers from compressed air to steam operation (Tombs 1996).

Richborough Generating Station was closed in March 1996, and Ince Generating Station was closed in March 1997, both due to financial considerations (PowerGen 1998a, 1998b).

Energie-Versorgung Schwaben Marbach III Power Plant
Trial testing of Orimulsion operation was conducted at the Energie-Versorgung Schwaben AG Marbach III Power Plant in Marbach, Germany in 1993. The emissions tests associated with the trials were different than those conducted in other locations, as they focussed on the impacts on ambient pollutant concentrations. The trials lasted for 16 days, with ambient measurements of CO, NO_2, SO_2, HCl, PM, metals, and dioxins and furans being taken during that period. Calculations were made to estimate the contribution of the plant to the background during operation with Orimulsion. Contributions to the ambient pollutant concentrations were determined to be significant if they were greater than 1% of the limit, guide, or target value (collectively referred to as appraisal value) set by the local air pollution authority or if they were 10% of the background or "preliminary" pollution level. Table 3-8 shows the appraisal value, the maximum contribution from emissions during Orimulsion operation, the percent contribution from Orimulsion emissions, and the background ambient pollutant concentration. As seen in the table, only Ni and V reported to be from Orimulsion operation were of concern in terms of the criteria noted above, and only SO_2 and precipitated PM, Ni, and V were greater than 0.1% of the appraisal value (TÜV Südwest 1993).

Planned Operations
This section describes testing or studies conducted for plants that have planned for use of Orimulsion. In some cases, these plans were not carried out, but the information presented here remains relevant to evaluating the differences between Orimulsion and other fossil fuels. Plans were made to convert the Florida Power & Light Company Manatee Plant from heavy fuel oil to Orimulsion in 1998. The Manatee Plant consists of two 800 MWe units designed for firing heavy fuel oil. Changes in the heat transfer characteristics due to the higher fuel water content and the nature of the ash deposited on boiler surfaces would have required modifications to the boiler and to the fuel receiving, storage, and handling system. These changes would have resulted in a derating of the unit by approximately 8% (Blum et al. 1998).

Additional pollution controls were also planned for the plant. The existing multicyclone particle collectors were to be replaced with ESPs for PM control, and a wet limestone scrubber was to be added as an FGD system. The ESP was designed to remove approximately 94% of the PM generated by Orimulsion 100 combustion to meet an emission rate of 0.02 lb/10^6 Btu. The FGD system was designed to control approximately 95% of the uncontrolled SO_2 concentrations, with a target emission rate of approximately 0.22 lb/10^6 Btu. NO_x controls for the units were to consist of low

Table 3-8. Comparison of long-term contributions to ambient concentration or deposition of pollutants from the combustion of Orimulsion 100 at Marbach III Power Plant to appraisal values and background concentrations or deposition during trial tests of Orimulsion combustion (TÜV Südwest 1993).

Pollutant	Unit	Appraisal Value	Maximum contribution from Orimulsion operation	% contribution of Orimulsion emissions to appraisal value	Background concentration
CO	$\mu g/m^3$	10,000	0.002	0.00002	1000
NO_2	$\mu g/m^3$	80	0.024	0.03	40
SO_2	$\mu g/m^3$	140	0.22	0.16	20
Suspended PM	$\mu g/m^3$	150	0.009	0.006	50
Precipitated PM	$g/(m^2\,d)$	0.65	0.0007	0.11	0.18
PCDD/F	pg/m^3	0.016	0.00009	0.056	0.01-0.02
HCl	$\mu g/m^3$	100	0.0002	0.0002	10
Hg	ng/m^3	1000	0.00018	0.00002	3
As in suspended PM	ng/m^3	5	0.00028	0.0056	7
Cd in suspended PM	ng/m^3	40	0.00019	0.0005	1
Cr in suspended PM	ng/m^3	7	0.0019	0.03	5
Co in suspended PM	ng/m^3	5000	0.0011	0.00002	1
Ni in suspended PM	ng/m^3	11	0.21	1.9	4
Pb in suspended PM	ng/m^3	2000	0.0037	0.0002	12
V in suspended PM	ng/m^3	-[1]	0.94	13.4[2]	7
Cd in precipitated PM	$\mu g/(m^2\,d)$	250	0.0003	0.006	< 0.5
Pb in precipitated PM	$\mu g/(m^2\,d)$	5	0.018	0.007	20

1. No value set.
2. % of background concentration.

NO_x burners in combination with reburning. The reburning system was designed to use Orimulsion 100 as the reburning fuel and to achieve an additional 47% reduction over the baseline emissions with LNBs alone. The NO_x control technologies were designed to achieve an emission rate of 0.1255 lb/10^6 Btu (Blum et al. 1998).

Reburning Development
Full-scale testing of Orimulsion 100 as a reburn fuel was conducted at Illinois Power Company's Hennepin Power Station in 1997 (Rostorfer et al. 1997, 1998). Hennepin Unit 1 is a 74 MWe tangentially-fired unit burning an Illinois #6 coal. The unit became operational in 1953, and had been the site of a U.S. DOE Clean Coal Technology project to demonstrate natural gas reburning as a NO_x control technology (Folsom 1995). The Orimulsion reburn project required several modifications to the plant to allow Orimulsion to be used on Unit 1, since the unit was not designed to use liquid fuels. The barge used to transport the Orimulsion was used as the storage tank, and temporary heat-traced insulated fuel lines were installed to move Orimulsion from the barge to the plant. A Moyno positive displacement pump was used as the fuel supply pump. Four Orimulsion injectors were installed in three corners of the boiler, with the fourth corner having only three

The Orimulsion reburn tests achieved a 64% NO_x reduction at the Hennepin Station at a 16% reburn fuel injection rate. NO_x emissions were reduced from a baseline value of 0.75 lb/10^6 Btu to a level of 0.27 lb/10^6 Btu during continuous testing over nearly one full day. This compares with a reduction of 67% (to 0.24 lb/10^6 Btu) when using natural gas as the reburn fuel. OFA capacity at the plant limited the reburn rate to 16% for Orimulsion, but modeling predictions indicated further reductions were possible at higher reburn rates if additional overfire air capacity could be obtained. Loss on ignition values were noted as being "within the range of typical plant experience" (Rostorfer et al. 1997, 1998). Figure 3-14 shows the results of short-term reburn testing at Hennepin, and shows NO_x emission rates during baseline operation, use of OFA only, and reburning with natural gas and Orimulsion. Figure 3-15 presents NO_x emission rates as a function of % reburn fuel injection for natural gas and Orimulsion.

A general overview of reburning with Orimulsion was discussed by Schimmoller (1998). This article states that the capital costs associated with reburning are estimated at between $15 and $20/kW, which was noted as being cost effective in comparison with other NO_x control technologies. The use of Orimulsion as a reburning fuel was estimated as being more cost effective than natural gas and to provide greater NO_x reductions than coal. Depending upon the price differential between Orimulsion and natural gas, annual costs can be similar to overfire air or selective noncatalytic reduction (Schimmoller 1998).

Engineering Studies
Several engineering and feasibility studies have also been conducted to evaluate the use of Orimulsion in existing plants and to evaluate potential performance of pollution control systems for Orimulsion applications. These studies are primarily analytical in nature as opposed to experimental, but provide additional information on the potential for emissions control in Orimulsion-fired plants.
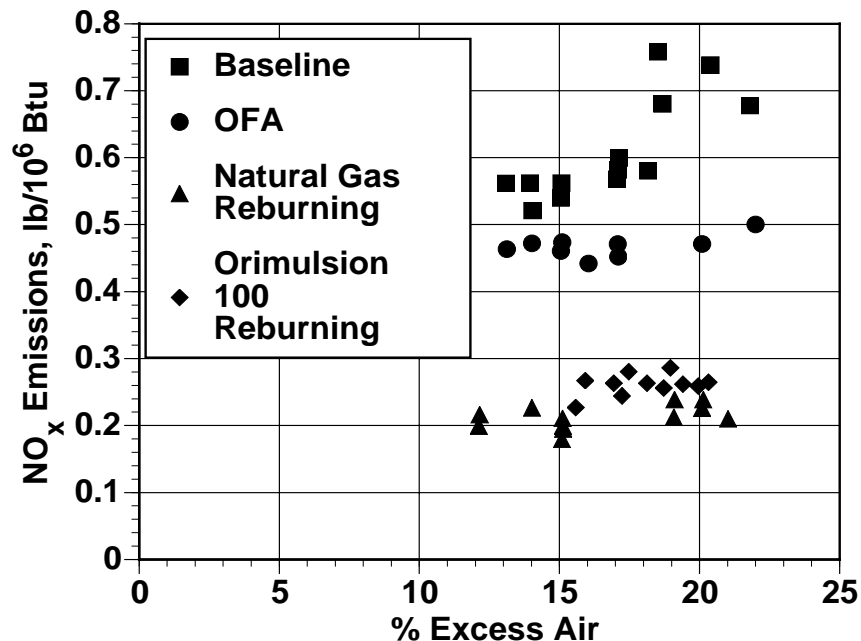
Figure 3-14. NO_x emissions measured during the reburning demonstration at Hennepin Station. Baseline emissions, emissions with overfire air only, and emissions using natural gas and Orimulsion 100 as reburn fuels are shown (Rostorfer et al. 1997).
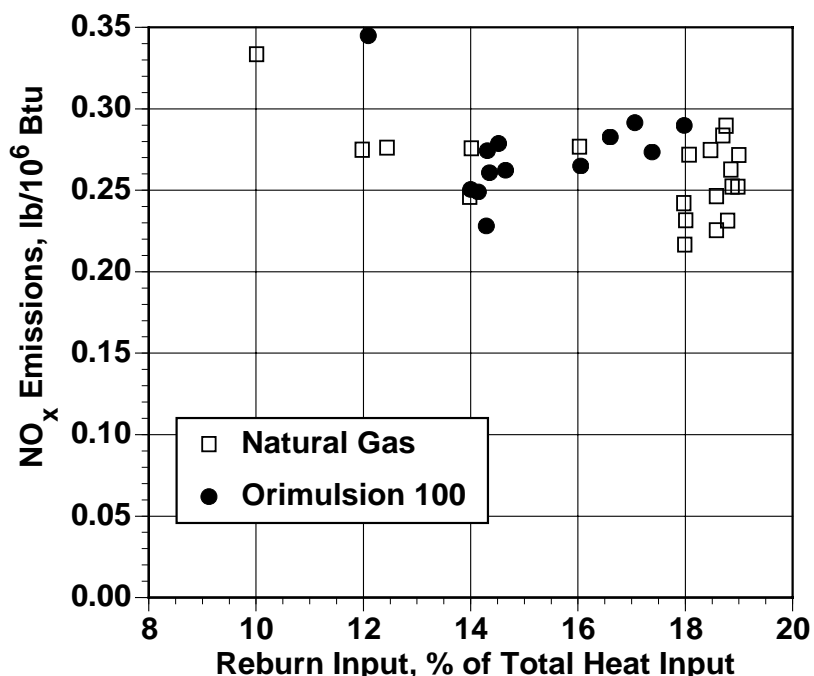
Figure 3-15. NO_x emissions measured during the reburning demonstration at Hennepin Station using natural gas and Orimulsion 100 as reburn fuel, as a function of % reburn fuel input (Rostorfer et al. 1997).

Feasibility Studies

Energy and Environmental Research Corporation (EERC) conducted a feasibility study with Intevep, the research arm of the Venezuelan petroleum company Petroleos de Venezuela, S.A. (PDVSA) to evaluate the technical and cost aspects of converting a small utility plant to Orimulsion. The study evaluated the conversion of a two-unit plant firing heavy fuel oil to Orimulsion. The plant evaluated had two 105 MWe tangentially-fired boilers, designed and built in the late 1950s, with ESPs installed for PM control.

The study evaluated operational, economic, and environmental impacts of the conversion, and concluded that the conversion could be made without reducing the plant's rating while meeting all applicable environmental regulations, and with a return on investment of 27.8%. The conversion specified the installation of a wet FGD system to meet the applicable SO_2 emissions limits, modification of the burner atomizers, increased sootblowing capacity, new induced draft fans to meet the greater volume of flue gas and the higher pressure drop with the FGD system, and improved instrumentation and control systems (EER/Intevep undated).

An in-depth feasibility study evaluating the conversion of New England Electric Company's Salem Harbor Station to Orimulsion was conducted, and evaluated a number of different alternatives from conversion of a single unit to conversion of all four units at the plant. Several alternative pollution control configurations were also considered in the study. For a conversion of the 440 MWe Unit 4 alone, it was determined that a wet limestone FGD system would eventually be required to achieve a 93% reduction in SO_2 emissions and a selective catalytic reduction (SCR) system would be required to achieve 76% NO_x reductions (both reductions based on uncontrolled levels). In addition, a wet ESP was recommended for control of any visible plumes associated with emissions of SO_3. The final proposed design also included wastewater treatment facilities, production of gypsum from the scrubber solids, and extensive boiler modifications to maintain unit rating and heat rate. Other options included the installation of a reburning system upstream of the SCR to reduce the cost of NO_x controls and modification of the ash handling system to allow for the different characteristics of Orimulsion fly ash. The feasibility study determined that applicable air pollutant emission limits

could be met when using Orimulsion if appropriate pollution control equipment were installed (Lentjes Bischoff 1997). Currently, the Salem Harbor Station is not actively considering conversion to Orimulsion.

A more general overview of issues associated with conversion to Orimulsion was conducted by Bechtel Corp. (Khan 1996). This study found that converting to Orimulsion from heavy fuel oil would result in an economic break-even for a plant that had a 33% capacity factor if the capital cost of conversion was $167/kW. For a capital cost of $250/kW, the break-even capacity factor was estimated at 48%. For capacity factors above these points, the plant would generate a net savings. The study also noted that more effective environmental controls were likely to be required when using Orimulsion than when using heavy fuel oil, but that emissions regulations could be met with proper pollution control equipment. The study also noted that a plant that converted to Orimulsion would be likely to face more stringent emissions limits, since units that repower may be required to meet new source performance standards or controls for prevention of significant deterioration (Khan 1996).

Pollution Control Equipment Analyses
All of the Orimulsion-fired plants reporting a reduction of SO_2 emissions by FGD employ wet limestone forced oxidation (WLFO) systems, with the exception of the Mitsubishi unit, which uses a Wellman-Lord process that was in place prior to conversion to Orimulsion (Olen 1998b). The extensive industrial experience with WLFO scrubbers and the ability of these systems to produce gypsum as an end product have made them the preferred system for application to Orimulsion-fired boilers. However, an analysis of lime spray dryer FGD designs indicate they may be competitive on a cost basis with WLFO systems for units with high sulfur emissions over the life of a plant. One of the difficulties associated with spray dryer designs is the production of calcium sulfite, which has no commercial value and must be landfilled, in contrast to the salable gypsum produced by WLFO systems. Mixing Portland cement with the spray dryer solid waste was evaluated to determine whether such a mixture could stabilize the wastes physically and chemically. At 10% mixture of cement with spray dryer waste was determined to result in the best physical characteristics (density, hardness) and the lowest leachability of constituents such as Ca, V, and sulfates (Kuchibotla et al. 1998). To date, no plants are known to be considering spray dryers for FGD.

Other Work
The studies below do not have direct application to Orimulsion use in utility boilers, but are included to demonstrate the range of work that has been conducted on applications of Orimulsion.

Diesel Engines
Orimulsion has been tested in diesel engines, but no emissions data are currently available from these tests. The tests were intended to evaluate whether Orimulsion could be used as a diesel engine fuel, and were tested in three different low- and medium-speed engines (Marruffo and Sarmiento 1997).

Gasification
Orimulsion has been evaluated by researchers in the U.S. and Japan as a feedstock for gasification processes. In the U.S. study, Orimulsion was found to be a better feedstock than coal-water slurries, as measured by the volume of product gas per unit fuel or per unit O_2 required (Quintana and Davis 1990). The U.S. tests were conducted over a 9-day period, with 144 tons of Orimulsion gasified (Marruffo and Sarmiento 1997). Few details were available regarding the Japanese work, but no significant problems in using Orimulsion as a gasification feedstock were reported (Inumaru et al. 1993).

Briquetting of Coal Fines
Coal cleaning operations produce a waste product consisting of water and relatively high levels of fine coal particles. It is desirable to recover these coal fines for use as a fuel. However, the large surface areas and high water contents make it difficult to dewater the fines in preparation for production of pellets. Orimulsion has been evaluated as a binding agent, and the results of these tests

indicate that it can be effectively used in the coal fine dewatering and pelletizing process (Kan et al. 1998). This process of adding a bitumen to the coal fines before dewatering, called GranuFlow™, was developed by the Department of Energy's Federal Energy Technology Center (FETC), and has been demonstrated at FETC and several commercial-scale coal cleaning plants. (Wen and Killmeyer 1996, Zitron et al. 1998).

Cement Kilns
Tests were conducted at the Arawak Cement Company in Barbados to evaluate the use of Orimulsion as a fuel in cement kilns. One evaluation of the tests stated that Orimulsion could be used without additional emissions control equipment because the higher SO_2 generation of the fuel would be offset by the reaction of the sulfur with the cement clinker (Marruffo and Sarmiento 1997). The cement company has since begun commercial operation using Orimulsion (Bitor America 2000).

Desulfurization
A study of hydrodesulfurization of both Orinoco bitumen and Orimulsion was conducted using several Ni and molybdenum catalysts. The catalytic treatments removed up to 75% of S in the bitumen and up to 58% of S in Orimulsion (Sharma and Olson 1995).

Summary of Previous Work
This section will summarize the results reported from the various studies discussed above to provide an overall view of the performance of Orimulsion related to operations and emissions. Summary plots and tables for several pollutants are included for as much of the existing data as possible.

Operational Issues
Fuel Handling and Atomization
As noted in the previous chapter, Orimulsion is highly sensitive to extremes of temperature and excessive shear rates during handling. Exceeding the recommended storage and handling limits on these parameters may lead to a breakdown of the emulsion and poor combustion performance. The characteristics of the fuel make it important to select the proper atomizing nozzle and approach to ensure the fuel does not degrade. While many units that fire heavy fuel oil use mechanical atomization, plants that have converted from heavy fuel oil to Orimulsion have also converted their fuel atomizers to use steam rather than mechanical pressure. Poor atomization may lead to poor burnout or flame instability and increased emissions of CO, unburned carbon, or NO_x.

Excess O_2
In general, plants using Orimulsion tend to operate at somewhat lower excess O_2 levels than plants using heavy fuel oil, and at significantly lower excess O_2 levels than plants using pulverized coal. For example, Ince Generating Station was able to consistently operate at O_2 levels less than 0.1% in the stack with carbon-in-ash levels of less than 0.5%. O_2 levels are reduced to the lowest point consistent with acceptable CO and unburned carbon to minimize the amount of SO_3 formation and to improve boiler thermal efficiency.

Boiler Efficiency
Boiler efficiency depends upon several factors, including the efficiency of converting carbon in the fuel to CO_2, the heat transfer efficiency of the boiler tubes, and the mass of flue gas exiting the boiler. Each of these can be affected by converting to Orimulsion from other fuels. Carbon conversion efficiency when firing Orimulsion tends to be very high and, based on unburned carbon in ash measurements, tends to be higher than for heavy fuel oil. For both fuels, however, carbon conversion efficiency is usually greater than 99% and may approach 99.9% in well-operated systems. Orimulsion has been shown to result in reduced boiler tube heat transfer and reduced efficiency due to more solid deposits than are typically observed during heavy fuel oil use. The high water content of Orimulsion significantly impacts boiler thermal efficiency by adding a substantial mass of a chemically inert compound to the flue gas mass, resulting in greater levels of heat being carried out of the boiler rather than being transferred to the steam. While Orimulsion usually requires less excess O_2 and therefore less air into the boiler to maintain acceptable CO and unburned carbon, the resulting

O_2 and therefore less air into the boiler to maintain acceptable CO and unburned carbon, the resulting reduction in flue gas mass is not great enough to overcome the increase from the water in the fuel. Boiler efficiency changes measured during the Dalhousie Orimulsion 100 demonstration tests showed a reduction of boiler efficiency from 87.2% when firing heavy fuel oil with a clean boiler to 84.5% when burning Orimulsion 100 with a clean boiler. When operating with a fouled boiler, the boiler efficiency dropped from 86.4% when using heavy fuel oil to 82.6% when using Orimulsion 100 (New Brunswick Power 1989). This efficiency drop may increase total mass emissions from a plant if it must operate at a higher fuel input rate to maintain output.

Boiler Fouling
As noted above, boiler fouling appears to be greater with Orimulsion 100 than when using heavy fuel oil, which can lead to reduced boiler efficiency. In addition, increased sootblowing to minimize the buildup of deposits can result in higher PM emissions during the sootblowing periods if the PM control equipment is not adequately designed to handle the increased inlet PM loadings. Finally, Orimulsion may use a Mg-based compound to help reduce the fouling properties of the fuel. In Orimulsion 100, this was mixed with the fuel prior to shipping, and with Orimulsion 400, the Mg compound is injected into the fuel just prior to its entering the burners. In both cases, this results in additional Mg emissions that are not associated with the hydrocarbon fuel itself.

Recent data indicate that the fouling associated with Orimulsion 100 use may be significantly reduced when using Orimulsion 400. The Asnaes Power Station has experienced reduced levels of boiler fouling when using Orimulsion 400, and has thus been able to achieve long term operation at 625 MW versus the 610 MW achievable using Orimulsion 100. Unit 5 is currently limited to 625 MW due to reheater temperature limitations rather than due to boiler tube fouling. The plant planned to cease any injection of Mg-based reagents based on the results of several months of operation with Orimulsion 400 (Miller and Shores 1999).

Air Emissions
CO
CO emissions are strongly influenced by the excess O_2 levels at which a plant is operated. Emission concentrations as low as 30 ppm have been reported during full-scale operation. Significantly higher CO emission concentrations are likely as O_2 levels drop below those generally reported in the literature, with one instance of emission concentrations as high as 1000 ppm reported. Table 3-9 presents a summary of reported CO emission concentrations from both full- and pilot-scale tests. In general, CO emission concentrations seem to be the same or slightly lower when using Orimulsion than when using heavy fuel oil, although conditions and equipment differences at individual plants may result in Orimulsion CO levels being higher than those from heavy fuel oil.

NO_x
NO_x emissions measured when firing with Orimulsion are reported to be slightly higher than those measured when firing with heavy fuel oil and lower than those measured when firing coal at full

Table 3-9. CO emissions measured during pilot- and full-scale tests for heavy fuel oil and Orimulsion 100.

Plant or test	Scale	O_2 Level During Test	CO (using Heavy Fuel Oil)	CO (using Orimulsion 100)
Dalhousie #1 Demonstration Tests (New Brunswick Power 1989)	Full	0.7%	60 ppm	30 ppm
Osaka No. 4 (Kaneko et al. 1996)	Full	0.7 - 3.0%	100 ppm	100 ppm
PowerGen (Allen and Beal 1996)	Pilot	0.3-1.2%	30-45 ppm	33-36 ppm
Hungarian Power (Barta et al. 1996)	Pilot	1%	40 ppm	61 ppm

scale. Reported NO_x measurements taken during firing of Orimulsion 400 indicate that use of Orimulsion 400 may result in slightly lower NO_x emissions than those from the firing of Orimulsion 100. Pilot- scale studies tended to indicate Orimulsion firing reduces NO_x emissions compared to those from firing heavy fuel oil. These results are summarized in Table 3-10. Differences in operating conditions and burner performance can significantly impact NO_x emissions. Conditions that are appropriate for heavy fuel oil or coal firing may not be optimum for operation using Orimulsion. Further discussion of NO_x emissions and the use of low NO_x burners will be presented below.

SO_2 and SO_3

Uncontrolled SO_2 emissions are primarily dependent upon the sulfur content of the fuel. Orimulsion's high sulfur content results in uncontrolled SO_2 emissions of approximately 2500 ppm, consistent with uncontrolled SO_2 emissions from other fuels with similar sulfur contents. Once formed, control of SO_2 is fundamentally the same for Orimulsion as for other fuels, and there has been no report of any difference in achieving adequate SO_2 control when using Orimulsion compared to other fuels.

SO_3 emissions are a consequence of the fuel sulfur content and the high level of V, which acts as a catalyst to promote formation of SO_3 from SO_2, particularly when there is adequate O_2 for the reaction to occur. SO_3 emissions are reduced to some degree by operating at low excess O_2 and by

Table 3-10. NO_x emissions measured during pilot- and full-scale tests for heavy fuel oil and Orimulsion. Unless otherwise noted, the post-conversion fuel is Orimulsion 100 and all values are corrected to 3% O_2.

Plant or test	Scale	Pre-conversion NO_x and fuel	Post-conversion NO_x
Dalhousie #1 Demonstration Tests (New Brunswick Power 1989)	Full	180-190 ppm Heavy fuel oil	180-215 ppm
Dalhousie #1 and #2, using Orimulsion 400 (Irvine and Eagles 1998)	Full	125 ng/J Orimulsion 100	105-110 ng/J (Orimulsion 400)
Osaka No. 4 (Kaneko et al. 1996)	Full	120 ppm Heavy fuel oil	200 ppm (uncontrolled)
Asnaes Unit 5 (SK Energy undated)	Full	250 ppm(1) Coal	150-180 ppm
Asnaes Unit 5, using Orimulsion 400 (Gibb 1999)	Full	150-180 ppm Orimulsion 100	80-160 ppm Orimulsion 400
Sanford Unit 4 (Entropy 1991)	Full	NM	400 ppm
PowerGen (Allen and Beal 1996)	Pilot	420 ppm Heavy fuel oil	390 ppm
Hungarian Power (Barta et al. 1996)	Pilot	270 ppm Heavy fuel oil	220 ppm
ENEL (XCL burner) (De Santis et al. 1996)	Pilot	410 mg/Nm^3 Heavy fuel oil	190 mg/Nm^3
ENEL (TEA burner) (De Santis et al. 1996)	Pilot	240 mg/Nm^3 Heavy fuel oil	320 mg/Nm^3

1. O_2 level not reported.

the use of Mg-based additives. Table 3-11 shows the reported SO_3 emissions from full- and pilot-scale tests.

PM

Particulate matter emissions from Orimulsion depend upon the ash content of the fuel, the carbon burnout, and to a slight degree the formation of SO_3 aerosols. The PM generated by the combustion of Orimulsion tends to be very small, with the majority of the particle mass less than 1 μm in diameter, and in some cases with the majority of particle mass less than 0.3 μm in diameter. Orimulsion PM contains substantial levels of Mg, Ni, and V that have been reported as being highly water soluble, resulting in potential difficulties in disposal in landfills due to subsequent leaching of these metals. The captured fly ash has been reported as being much less dense than the fly ash generated from the combustion of heavy fuel oil, resulting in problems in solid handling and transport. In some cases, the addition of water to the ash after collection has been shown to substantially increase the ash density and its potential for high wind-borne fugitive emissions during transport and storage. Orimulsion PM has resistance sufficient to allow it to be controlled using ESPs (discussed in more detail below).

Comparisons of PM emissions from Orimulsion operation with those from heavy fuel oil or coal will be highly dependent upon the characteristics, particularly the ash content, of the other fuel being used. Table 3-12 presents the PM emissions reported from full- and pilot-scale tests of Orimulsion use. Comparisons of PM size distributions is also highly dependent upon operating parameters such as fuel atomization (a function of fuel flow and temperature and atomizing method), making general comparisons between different fuels difficult if not impossible. Table 3-13 presents reported PM size distributions for Orimulsion and heavy fuel oils burned in the same units.

Hazardous Air Pollutants and Metals

Substances considered to be hazardous air pollutants (HAPs) are listed in Title III of the 1990 Clean Air Act Amendments (CAAAs), which includes 189 compounds and compound classes (Clean Air Act 1990). As seen in the above discussions, the emphasis on HAP measurements has been oriented

Table 3-11. Reported SO_3 emissions measured during pilot- and full-scale tests for heavy fuel oil and Orimulsion. Unless otherwise noted, the post-conversion fuel is Orimulsion 100.

Plant or test	Scale	Pre-conversion SO_3 and fuel	Post-conversion SO_3
Dalhousie #1 Demonstration Tests (New Brunswick Power 1989)	Full	NM[1]	2-15 ppm
Osaka No. 4 (Kaneko et al. 1996)	Full	4-12 ppm (uncontrolled) Heavy fuel oil	44-68 ppm (uncontrolled)
Asnaes Unit 5 (SK Energy undated)	Full	NM	7.2 mg/Nm^3 Orimulsion 100
Asnaes Unit 5, using Orimulsion 400 (Gibb 1999)	Full	NM	1 ppm Orimulsion 400
Sanford Unit 4 (Entropy 1991)	Full	NM	0.0072 lb/10^6 Btu[2]
Hungarian Power (Barta et al. 1996)	Pilot	8.5 ppm Heavy fuel oil	13.2 ppm
ENEL (De Santis et al. 1996)	Pilot	NM	< 5 ppm

1. Not measured.
2. Sulfuric acid mist (including SO_3)

toward metals. This is consistent with the findings of EPA's Report to Congress on HAP emissions from utility boilers, which found that organic HAPs are not likely to be emitted from large utility boilers in significant amounts (EPA 1998). In addition to the measurements presented above, one study reported measurements of As, Cd, Pb, Hg, Ni, and V (not listed as a HAP in the 1990 CAAAs) and emissions of organic compounds including polycyclic aromatic hydrocarbons (PAHs), dioxins and furans, benzene, and formaldehyde. This study compared emissions from coal, heavy fuel oil, and Orimulsion, and concluded that HAP emissions from Orimulsion were lower than those for heavy fuel oil for all 10 compounds reported, and were lower than those for coal for 7 of the 10 reported compounds. Table 3-14 shows the measurements reported in this study (Allen and Beal 1997).

In general, HAP and metal emissions are generally low, even when uncontrolled. Emissions of V are consistently the highest trace element emission associated with Orimulsion. Concentrations of Ni and V in fly ash may result in difficulties in landfilling due to their high levels (10,000 ppm and higher) and the reported high water solubility of these compounds in the fly ash. Several efforts have been made to use the ash as a feedstock for V recovery, and this is currently being done by the Dalhousie Plant (Irvine and Eagles 1998).

CO_2

Emissions of CO_2 are important from the perspective of global climate change, but are not currently

Table 3-12. Reported PM emissions measured during pilot- and full-scale tests for heavy fuel oil and Orimulsion. Unless otherwise noted, the post-conversion fuel is Orimulsion 100.

Plant or test	Scale	Pre-conversion PM and fuel	Post-conversion PM
Dalhousie #1 Demonstration Tests (New Brunswick Power 1989)	Full	105 mg/Nm^3 (uncontrolled)	250 mg/Nm^3 (uncontrolled)
Osaka No. 4 (Kaneko et al. 1996)	Full	100-220 mg/Nm^3 (uncontrolled) Heavy fuel oil	180-300 mg/Nm^3 (uncontrolled)
Kashima-Kita (Olen and Alcantara 1993)	Full	NM(1)	280 mg/Nm^3 (uncontrolled)[2]
Asnaes Unit 5 (SK Energy undated)	Full	NM	12.1 mg/Nm^3 (controlled) Orimulsion 100
Asnaes Unit 5 using Orimulsion 400 (Gibb 1999)	Full	NM	3.3 mg/Nm3 (controlled) Orimulsion 400
Sanford Unit 4 (Entropy 1991)	Full	NM	0.16 lb/10^6 Btu (uncontrolled)
Ince "B" (Tombs 1996)	Full	NM	350 mg/Nm^3 (uncontrolled)
PowerGen (Allen and Beal 1996)	Pilot	0.05-0.1 lb/10^6 Btu Heavy fuel oil	0.3-0.35 lb/10^6 Btu (uncontrolled)
Hungarian Power (Barta et al. 1996)	Pilot	415 mg/Nm^3 Heavy fuel oil	160 mg/Nm^3 (uncontrolled)
ENEL (De Santis et al. 1996)	Pilot	NM	220-260 mg/Nm^3 (uncontrolled)

1. Not measured.
2. Measured without ammonia injection.

Table 3-13. Reported PM size distributions measured during pilot- and full-scale tests for heavy fuel oil and Orimulsion.

Plant or test	Scale	Pre-conversion PM size distribution and fuel		Post-conversion PM size distribution	
		% (by mass) < 10 µm	% (by mass) < 1 µm	% (by mass) < 10 µm	% (by mass) < 1 µm
Dalhousie #1 Demonstration Tests (NB Power 1989)	Full	75	45	98	80
		Heavy fuel oil			
Asnaes Unit 5 (SK Energy undated)	Full	NM[1]	NM	100	97
Ince "B" (Tombs 1996)	Full	NM	NM	Median diameter < 1 µm	
ENEL (De Santis et al. 1996)	Pilot	87.1	51.3	73.1	21.2
		Heavy fuel oil			

1. Not measured.

Table 3-14. Emissions of selected hazardous air pollutants from coal, heavy fuel oil, and Orimulsion, in $lb/10^{12}$ Btu (Allen and Beal 1997).

	Coal	Heavy Fuel Oil	Orimulsion
Arsenic	2.4	NA(1)	ND(2)
Cadmium	1.0	0.2	ND
Lead	3.7	3.9	0.18
Mercury	6.4	5	ND
Nickel	21	123	3.7
Vanadium[3]	NA	141	125
PAH	$6x10^{-4}$	0.013	ND
Dioxins/Furans	$2.5x10^{-6}$	$1.3x10^{-5}$	$3.5x10^{-6}$
Benzene	5.2	1.1	4.6
Formaldehyde	3.8	32	4.7

1. Not available
2. Not detected
3. Not on the list of HAPs in the 1990 Clean Air Act Amendments

regulated. Nevertheless, given the level of concern regarding the potential for global climate change, Orimulsion has been evaluated for its potential for CO_2 emissions compared with coal and heavy fuel oil. Because Orimulsion has a higher hydrogen to carbon ratio than coal, the amount of CO_2 emitted during combustion of Orimulsion will be lower than that emitted during the combustion of coal. This characteristic of Orimulsion has been exploited at the Asnaes Power Station. Asnaes staff report that the plant emits 16% less CO_2 using Orimulsion 400 than was emitted when burning pulverized coal. This difference, in combination with the plant size, is large enough to account for 1/20 of the Danish government's national goal of 20% CO_2 reduction (Miller and Shores 1999).

An extensive study of the use of Orimulsion in integrated gasification combined cycle (IGCC) power

and chemical plants and the capture of CO_2 in these systems was carried out by Parsons (1997) for the International Energy Agency (IEA). This study compared CO_2 emissions for several scenarios of gasification and combined cycle operation using Orimulsion as a feedstock, and did not compare Orimulsion to other fuels. An IEA summary of the study noted that the emissions of CO_2/kWh generated from Orimulsion in an IGCC were lower than those of coal but higher than those of natural gas (Parsons 1997).

Air Pollution Control

The pollutant concentrations generated by the combustion of Orimulsion are such that some degree of air pollution control will be required, although the level of control is likely to vary according to the requirements of individual locations. It is important, then, to understand whether available control technologies can be used to reduce emissions from the combustion of Orimulsion to an acceptable level. This section will discuss the reported experience with applying air pollution control technologies to plants firing Orimulsion.

NO_x Control

NO_x concentrations can be controlled using a number of technologies, divided into two main types - combustion controls and post-combustion controls (Muzio and Quartucy 1997). The combustion controls are those that rely on alteration of the combustion conditions to minimize formation of NO_x in the combustion zone, while post-combustion technologies convert NO_x already formed to nitrogen or other products. Combustion controls are much more sensitive to changes in fuel properties, although the presence of specific compounds can also adversely impact the performance of post-combustion NO_x controls.

Both low NO_x burners (LNBs) and reburning have been evaluated for use in plants using Orimulsion, while the only reported post-combustion technology used at Orimulsion-fired plants is selective catalytic reduction (SCR). Reported results indicate that each of these technologies can be successfully applied to control NO_x from Orimulsion combustion, although the designs of the technologies must account for the specific characteristics of the fuel. In this respect, Orimulsion is similar to other fuels in that fuel-specific and site-specific factors must be taken into account when designing and operating NO_x control equipment. The particular technology or combination of technologies used at a specific plant will depend upon factors such as cost and required NO_x emission level.

Low NO_x Burners

Pilot-scale tests have verified that NO_x emissions from Orimulsion combustion can be controlled using the same techniques used for low NO_x combustion with other fuels. Staged combustion methods used in low NO_x burners (LNBs) for other fuels have been demonstrated for Orimulsion, resulting in NO_x reductions similar to those measured using other fuels (De Santis et al. 1996, Allen and Beal 1996, Quig and Woodworth 1997). In general, LNBs can achieve 30-50% reduction of NO_x from baseline emissions.

Reburning

Reburning has been demonstrated at a full-scale plant, using Orimulsion as a reburn fuel. Emission reductions of greater than 60% were demonstrated on a unit burning coal as the base fuel. Reported pilot-scale testing of reburning using Orimulsion as the reburn fuel have confirmed its ability to be used as a reburn fuel, and measurements of Orimulsion reactivity also support its use in such applications. Orimulsion reburn installation costs have been estimated at approximately $15/kW (Rostorfer et al. 1997).

Selective Catalytic Reduction

In cases where very high NO_x reductions are required, selective catalytic reduction (SCR) may be used on Orimulsion-fired units. This type of system was installed at the Osaka No. 4 boiler in Japan, allowing the unit to reduce its uncontrolled emissions to less than 30 ppm, an 85% reduction from the uncontrolled NO_x emissions reported in Table 9 (Hall and Lee 1998). One issue associated with SCR

use in Orimulsion-fired systems is the interaction between the ammonia (NH_3) injected for NO_x control and the SO_3 present in the flue gas. These can react to form particulate ammonium bisulfide, which can significantly increase the loading on the PM control equipment.

SO_2 and SO_3 Control

Control of SO_2 is achieved using conventional wet limestone forced oxidation scrubbers by all units currently burning Orimulsion. Several of these systems produce gypsum from the spent scrubbing liquor, minimizing the mass of solid waste that must be landfilled. SO_2 reductions of 90% or greater are typical of these systems, allowing controlled emissions of approximately 200 ppm to be achieved with conventional control methods. There have been no problems with scrubber operation unique to Orimulsion use that have been reported in the literature. The major issue associated with Orimulsion use when using scrubbers is the higher Ni and V contents of the scrubber sludge and gypsum. The Ni and V contents of these by-products have not been found to prevent either the sale of gypsum from Orimulsion or the safe disposal of scrubber sludge.

PM Control

In general, PM control can be achieved by using either ESPs or baghouses (fabric filters), although there have been no long term evaluations of baghouse performance on an Orimulsion-fired power plant. In general, however, either type of system should be applicable to Orimulsion, provided that the equipment is appropriately designed and operated.

ESPs

Uncontrolled PM levels of between 250 and 1,000 mg/Nm^3 are likely in units using Orimulsion, with the higher levels caused by the use of additives such as ammonia to the flue gas for neutralization of SO_3. PM from Orimulsion combustion is small in size, with 80-90% being less than 4 μm in diameter. Particle size distributions of Orimulsion PM (without flue gas additives) have typically been measured as having a bimodal distribution, with approximately 65% of the particle mass having a mean diameter of 0.4 μm and the remaining 35% having a mean diameter of 4.0 μm. Sootblowing tends to increase the amount of the larger size particles (approximately 4.0 μm in diameter) to result in roughly equivalent mass percent of the larger and smaller particle sizes (Olen 1998b).

PM control for utility plants burning Orimulsion has been demonstrated to be as high as 97% at the Kashima-Kita plant in Japan (Olen and Alcantara 1993). PM removal efficiencies of between 86 and 94% have been measured at other plants, with outlet emission rates ranging from 20 to 35 mg/Nm^3 (Irvine and Eagles 1998, Olen and Alcantara 1993). In some cases, existing ESPs have been modified by increasing the number of ESP fields or installing different discharge electrodes. These changes have improved performance over the original systems designed primarily for collection of PM from heavy fuel oil combustion. Other design and operational issues include an increase in flue gas volume due to higher water content of the fuel and higher furnace exit temperatures, increased ash resistivity, and higher inlet particle loading due to injection of ammonia or to boiler surface fouling. The low density of the collected ash requires some preparation of the ash to increase density and reduce fugitive dust; addition of water is usually adequate to solve these problems (Irvine and Eagles 1998, Tombs 1996). The reported data indicate that the design and operational problems can be addressed so that adequate PM control is achieved by ESPs, even in cases where high particle loadings result from injection of ammonia.

Baghouses

Pilot-scale tests of baghouse performance concluded that pulse jet baghouses may be suitable for use with Orimulsion if adequate protection of the bag materials was ensured. Such protection included the pre-coating of the bags with a sorbent material for low acid dewpoint operation, and co-injection of a sorbent material during high acid dewpoint operation. Similar tests of a reverse gas baghouse were inconclusive, primarily because of limited testing due to cessation of tests prior to completion of the expected test matrix. No full-scale operating unit currently uses baghouses for control of PM from Orimulsion.

Solid Residue Disposal

The ash generated by the combustion of Orimulsion and collected by PM control equipment tends to be less dense than that generated by the combustion of heavy fuel oils. In some instances, the procedures used to handle the captured ash required modification to improve handling capabilities. This typically involved the addition of a slight amount of water to the ash to increase density and improve ash particle agglomeration (Irvine and Eagles 1998).

The Ni and V contents of the captured ash are relatively high, and the ash can be processed to recover these elements. Ash from the Dalhousie Plant and from the Asnaes Generating Station is shipped to plants in the U.S. and Germany, respectively, for V recovery (Irvine and Eagles 1998, Miller and Shores 1999).

Chapter 4
EPA Pilot-Scale Experimental Approach and Equipment

A series of combustion tests were conducted at the NRMRL combustion research facilities in Research Triangle Park, NC to provide data on emissions from Orimulsion and heavy fuel oil generated in a single combustion system under controlled conditions.

Approach

The approach chosen for the test program was to measure emissions from the two formulations of Orimulsion and a commercially available heavy fuel oil in a single test combustor. This approach was believed to result in data that would allow direct comparison of the impact of the different fuels on air pollutant formation and emissions. By using this approach, changes in emissions due to different burner or combustor design parameters would be eliminated, and the only significant factors remaining would be the combustion conditions and the fuels.

Each test condition was run four times to allow the repeatability of the test condition and results to be quantified. Flue gas constituents and properties to be measured were CO, CO_2, NO_x, O_2, PM, SO_2, SO_3, and THC concentrations; particle size distributions; concentrations of As, Be, Cd, Cr, Cu, Fe, Mn, Mg, Ni, Sb, V, and Zn; and concentrations of volatile and semivolatile organic compounds. Table 4-1 shows the test matrix developed for the test program, with the number of measurements of each of the above constituents or parameters and the methods used in quantifying each constituent or parameter.

Test Equipment

All tests were conducted on a single research combustor under test conditions that were held as constant as possible. Some differences were anticipated due to differences in combustion characteristics between Orimulsion and heavy fuel oils. Operating at conditions appropriate to each fuel was viewed as more desirable than maintaining a single condition, since real world operation would adjust combustion conditions to achieve optimum performance based on the particular fuel. In particular, O_2 level was intended to be set based on the minimum O_2 that could be achieved without generating excessive CO. "Excessive" CO was defined to be approximately 50-100 ppm for these tests. To the extent possible, all other test conditions were intended to remain constant for all fuels.

Package Boiler Simulator

The package boiler simulator (PBS) is a $3x10^6$ Btu/hr horizontally-fired unit capable of burning natural gas or liquid fuels in an environment that simulates a water wall boiler. A schematic of the unit is shown in Figure 4-1. The PBS burner has an air-atomizing nozzle that is capable of handling the unit's full load heat input, based on No. 6 fuel oil. Since the PBS was operated at heat input rates well below full load, it was adequate to handle the higher volume of Orimulsion required to maintain a steady heat input rate. The PBS has a 10 in. inside diameter refractory lined burner section connected to a water cooled transition section of the same inside diameter. The transition section allows staged air or fuel injection through radial or axial ports or through two ports on the horizontal axis aligned 45° from the unit centerline. The transition section connects to the Dowtherm cooled boiler section, which has a 24 in. inside diameter and is 110 in. long. The combustion gases pass out of the boiler section to the vertical stack, where sampling ports are located for taking extractive samples. Inspection and access ports for injection probes or optical sampling are located along the boiler wall and at the stack end of the boiler.

Flue gases from the PBS are ducted to the facility's air pollution control system (APCS), which consists of a $4x10^6$ Btu/hr secondary combustion chamber, a fabric filter, and a wet acid gas scrubber. The APCS allows the PBS to operate under poor combustion conditions that intentionally generate higher than normal pollutant emissions during research studies without emitting those excessive pollutants to the environment. The PBS has been used in studies of low NO_x combustion and reburning for control of NO_x (Linak et al. 1985, Miller et al. 1998).

Table 4-1. Test matrix for EPA pilot-scale tests of Orimulsion air pollutant emissions.

Condition	1	2	3
Fuel	Orimulsion 100	Orimulsion 400	No. 6 Fuel Oil
Boiler Load (Btu/hr)	1,000,000	1,000,000	1,000,000
Excess O_2 (%)[1]	3	3	3
MgOH Injection	No	Yes	No
Number of test runs	4	4	4
CO, CO_2, NO_x, O_2, SO_2, THC (CEMs)	Continuous during test	Continuous during test	Continuous during test
PM concentration (Method 5)	3 tests	3 tests	3 tests
Particle Size Distribution (cascade impactor)	3 tests	3 tests	3 tests
Particle Size Distribution (SMPS)	1 test (5 or more runs per test)	1 test (5 or more runs per test)	1 test (5 or more runs per test)
Metal concentration (Method 29)	3 tests	3 tests	3 tests
Volatile Organic concentration (Method 0010)	3 tests	3 tests	3 tests
Semivolatile organic concentration (Method 0030)	3 tests	3 tests	3 tests
SO_3[2] (MACS train)	3 tests	3 tests	3 tests

1. Actual test O_2 level was intended to be set based on the minimum O_2 at which CO remained less than 50-100 ppm.
2. Miniature acid-condensation system (DeVito and Smith 1991)

Fuel Supply System

The fuel supply system can influence the stability of emulsified fuels such as Orimulsion. The system should minimize shear rates through pumps, piping, and fittings as much as possible, and should be able to maintain the appropriate temperature range during operation. The original fuel supply system used by the PBS was designed for heavy fuel oil and required modification before Orimulsion could be fed to the boiler. During operation with heavy fuel oil, the original fuel supply system (shown schematically in Figure 4-2) was used.

For operation with Orimulsion 100 and Orimulsion 400, the fuel supply system was modified to use a lower shear Moyno pump rather than the original gear pump and to eliminate the pressure relief valves and the continuous circulation loop used in the original supply system. The modified fuel supply system is shown in Figure 4-3.

A Mg-based additive was injected into the boiler during testing of Orimulsion 400. The additive was $Mg(OH)_2$, and was injected into the flame at a rate of between 0.35 and 0.54 g/min during operation at $1x10^6$ Btu/hr. This injection rate resulted in a molar ratio of between 2.1 and 3.8 mol Mg to 1 mol V in the fuel.

Instrumentation

The PBS has continuous emission monitors (CEMs) for measurement of combustion gas composition. Concentrations of CO, CO_2, NO_x, O_2, SO_2, and THC are measured by CEMs and
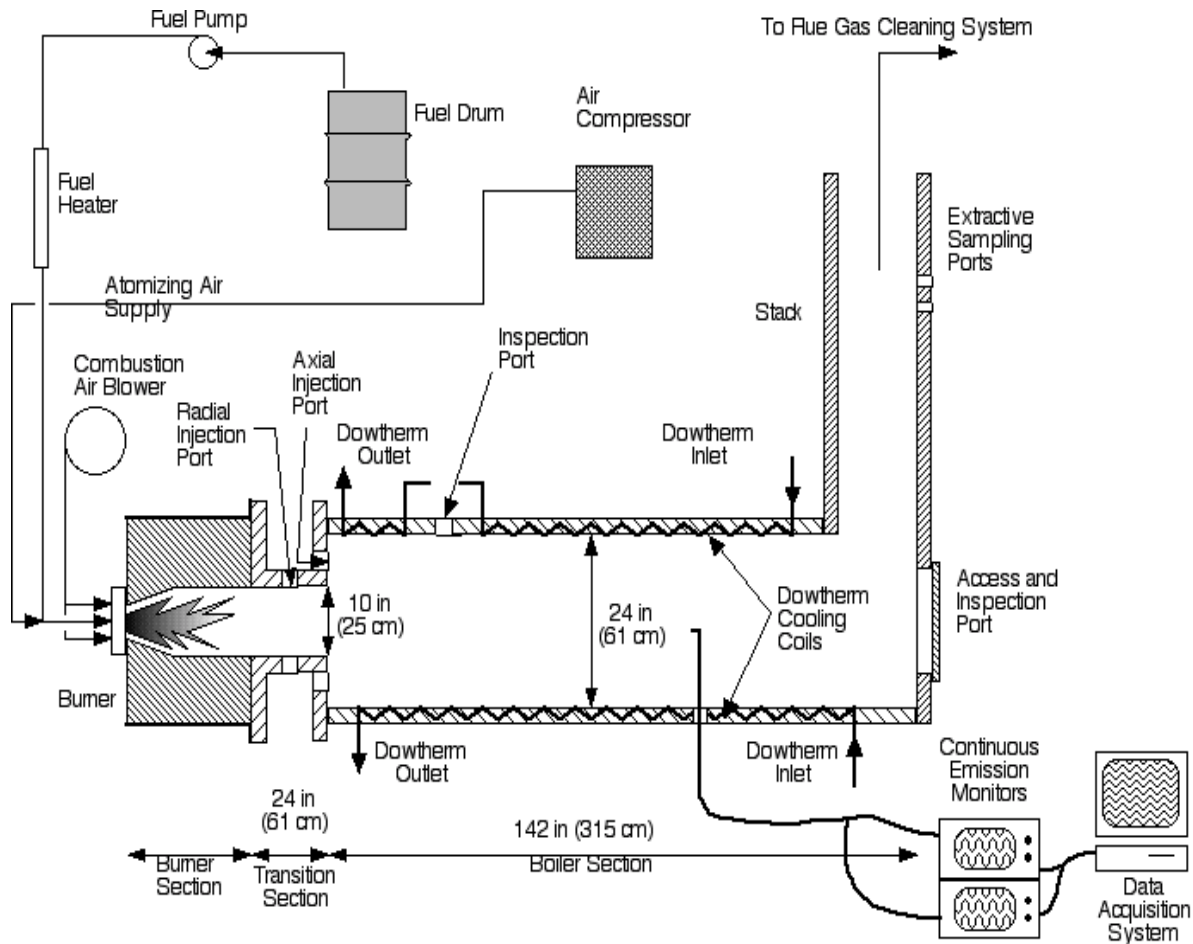
Figure 4-1. Schematic of Package Boiler Simulator.

continuously recorded using a computerized data acquisition system (DAS). Stack gases are extracted through a fixed stainless steel probe into Teflon® tubing and transported to the CEM sample conditioning system. The sample gases are dried using a Hankeson® dryer and particles are removed by a filter. A portion of the sample is then diverted to the NO_x analyzer, with the remaining sample passing through a Dryrite® canister and then to the other gas analyzers. THC measurements use a heated stainless steel sampling line that is maintained at 350 °F. The CEM system is shown schematically in Figure 4-4.

Continuous Emission Monitors
The CO and CO_2 analyzers were Rosemount® model 880A infrared analyzers. Two CO analyzers were used, one having an operating range of 0 to 1000 ppm (CO low) and one having an operating range of 0 to 5% (CO high). The CO_2 analyzer has an operating range of 0 to 20%. A Rosemount® model 951A chemiluminescence NO_x analyzer was used to measure concentrations of NO and NO_2 in the range of 0 to 1000 ppm. The analyzer can be used to measure either NO or NO_x. In the NO_x operating mode, the unit converts any NO_2 to NO prior to porting the gas to the detector. The analyzer was operated in NO mode during the test program

The O_2 analyzer was a Rosemount® model 755R paramagnetic analyzer, with a measurement range of 0 to 25%. SO_2 concentrations were measured using a Du Pont photometric model 400 analyzer. THC was measured using a Rosemount® 402 hydrocarbon analyzer, which operates using a flame
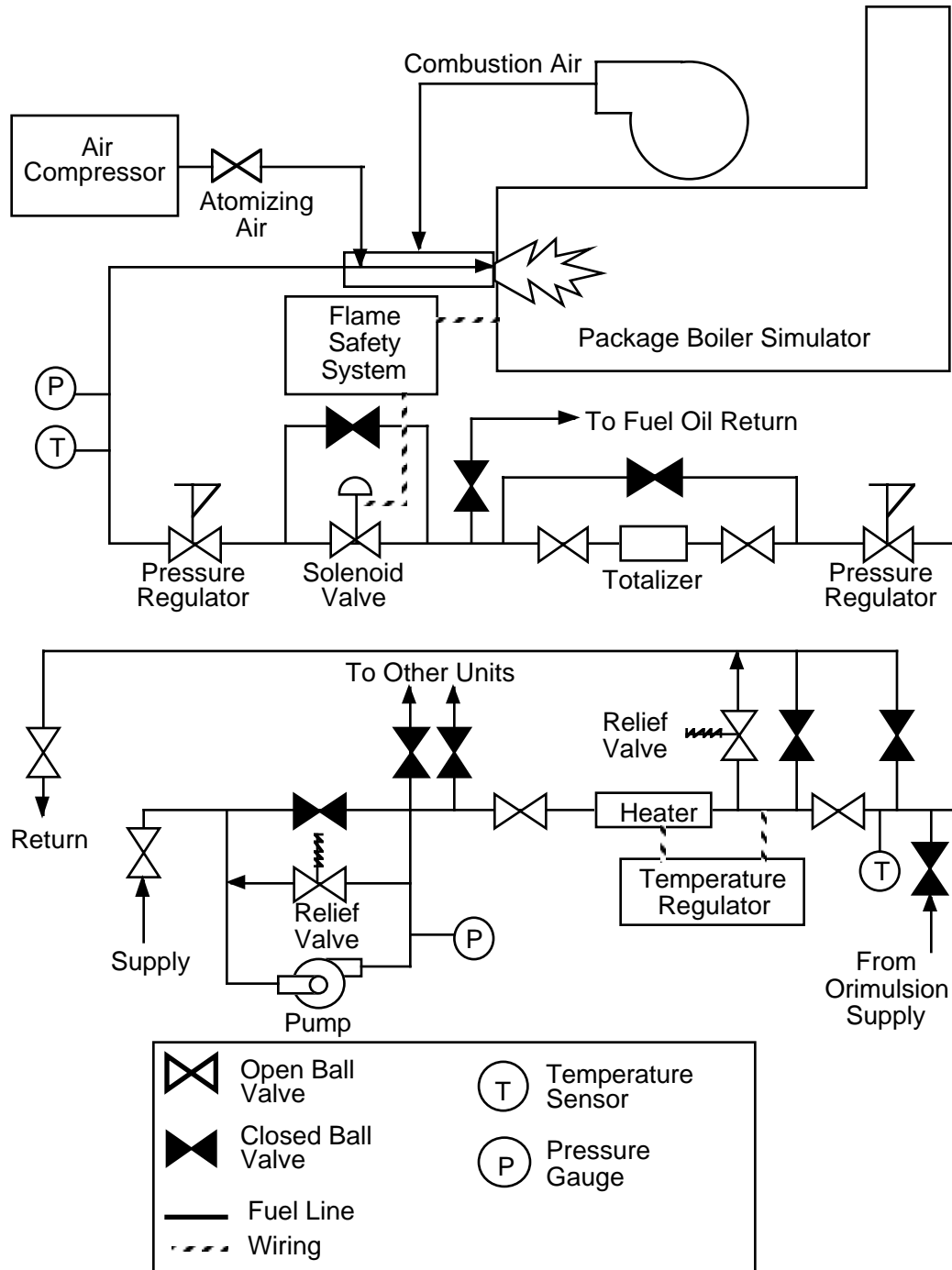
Figure 4-2. Schematic of fuel feed system for heavy fuel oil.

ionization detector. The THC measurement is given as equivalent methane (CH_4), and has an operating range of 0 to 50,000 ppm.

Data Acquisition System
The DAS is a computer-based system separate from the CEMs. It uses a Macintosh® computer and Strawberry Tree® data acquisition cards, and logs inputs from each of the CEMs at constant intervals
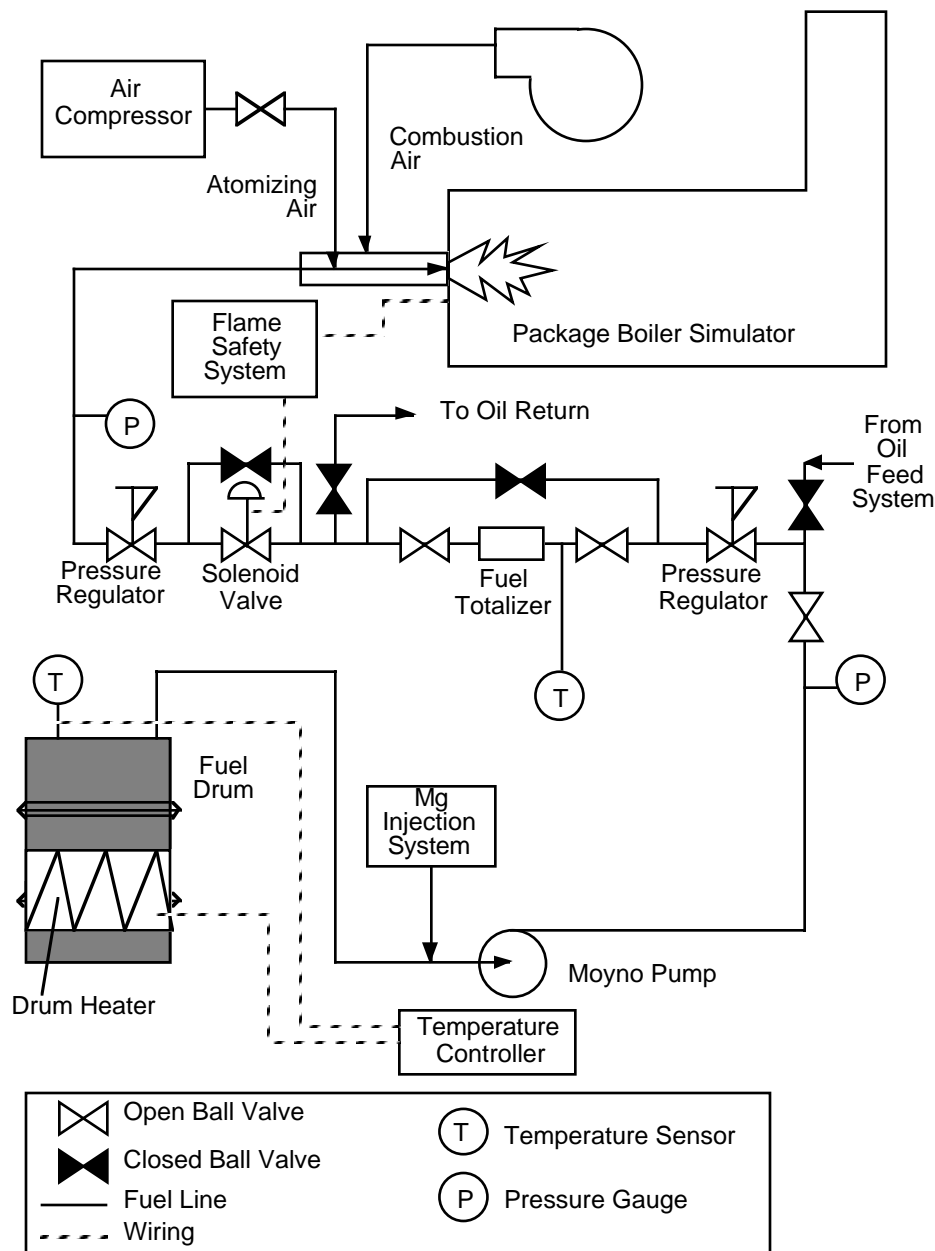
Figure 4-3. Schematic of fuel feed system for Orimulsion 100 and Orimulsion 400.

that can be adjusted according to the needs of each experiment. Selected data are shown on the screen during operation, and all data are stored on the unit's hard disk drive for later retrieval and reduction. Data logging is conducted only during testing or calibration.

Dilution Sampling System
A dilution sampling system (shown schematically in Figure 4-5) was used to collect samples for use in toxicity testing by EPA's National Health and Environmental Effects Research Laboratory (NHEERL). This system collects large quantities of PM for the toxicological studies. The system is capable of sampling 10 ft^3/min of flue gas. The sample passes through a modified Source Assessment Sampling System (SASS) cyclone and is then diluted with 100 ft^3/min of clean ambient
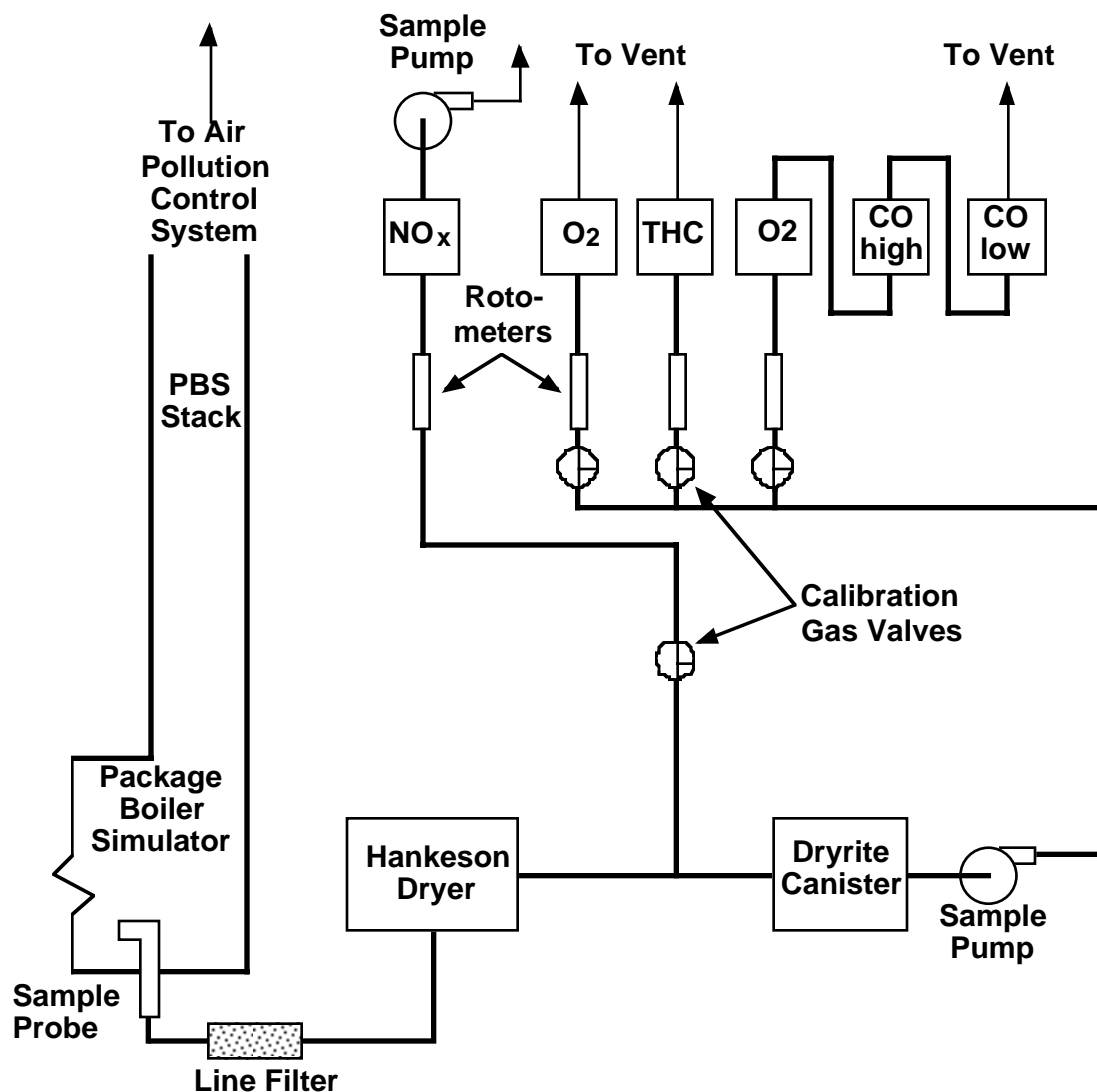
Figure 4-4. Schematic of continuous emission monitoring system.

air using a perforated cone assembly. Rapid uniform dilution cools the sampled gases and PM to nearly ambient temperature within a residence time of approximate 3 s. Isokinetic sampling conditions were not possible for these large dilution samples. Further details regarding the dilution sampler's construction and operation are presented by Steele et al. (1988).

The SASS cyclone preseparator produces 50 and 95% particle collection efficiencies at approximately 1.8 and 2.5 μm aerodynamic diameter, respectively, at standard conditions. The small fraction of PM that passes through the cyclone is collected on large (25.5 in. diameter) Teflon coated glass fiber filters for subsequent analysis (Linak et al. 1999).

Scanning Mobility Particle Sizer
A Thermo Systems, Inc., scanning mobility particle sizer (SMPS) was used to measure particle size
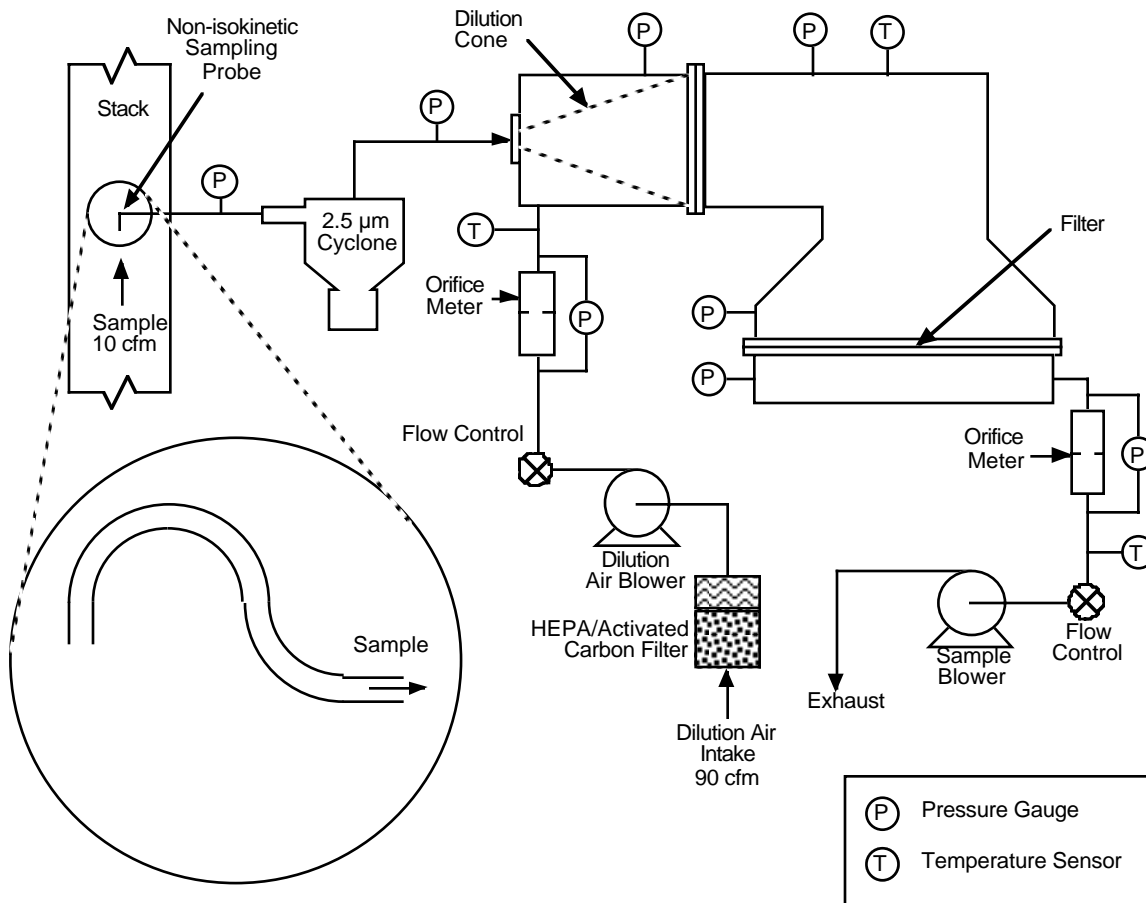
Figure 4-5. Schematic of high volume dilution sampling system.

distributions for particles with diameters in the range of 0.01 to 1.0 μm diameter. The SMPS classifies and counts particles using principles of charged particle mobility through an electric field. The SMPS was configured to yield 54 channels evenly spaced (logarithmically) over the operating size range. SMPS samples were extracted from the PBS stack isokinetically and diluted with filtered nitrogen (N_2) to a ratio of approximately 5 parts N_2 to 1 part stack gas. Dilution flow was controlled using a mass flow controller and total sample flow measured with a laminar flow element. Both devices were calibrated using a Gilabrator® bubble flow meter. Additional details of the system design and operation are described by Scotto et al. (1992) and Linak et al. (1994).

Scanning Electron Microscope
Samples were also collected on silver membrane filters and analyzed using a SEM equipped with an energy dispersive x-ray (EDX) spectrometer. These analyses provided morphological information of individual particles. Particles were extracted from the stack location using the same sampling system and dilution as used by the SMPS described above. However, these particles were directed through a stainless steel filter holder containing a 47 mm silver membrane filter. Sampling times of approximately 30-60 s provided a sufficient quantity of particles for analysis. Silver filters were used to improve conductivity and minimize particle charging caused by the electron beam.

Sampling Methods
EPA Methods 5 and 29
Particle concentrations were determined using EPA Method 5 (EPA 1994); EPA Method 29 was used to determine metal concentrations in the flue gases (Garg 1990). The particle concentration option

was used during the Method 29 operation, but the mercury option was not used, meaning that the Method 5 procedure used the same train as Method 29, allowing a single sampling train to be used to determine both PM mass and metal concentrations.

A blank Method 29 sampling train was prepared and set up at the sampling location, and remained at that location for the duration of sampling. The blank train filter was weighed, and the solutions were recovered and analyzed with the remaining Method 29 sampling trains to identify possible contamination. Two Method 29 trains were spiked with known concentrations of target metals and subsequently analyzed with the other samples to determine laboratory recovery of known concentrations. Chapter 11 (Quality Assurance) provides additional details concerning the blanks and spiked samples. The Method 29 samples were analyzed for As, Be, Cd, Cr, Cu, Fe, Mn, Mg, Ni, Sb, V, and Zn.

EPA Methods 0010 and 0030
EPA Method 0030 was used to sample the concentration of volatile organic compounds (VOCs) in the flue gases of all three fuels (EPA 1986a). EPA Method 0010 (sometimes referred to as a Modified Method 5) was used to sample semivolatile organic compounds for all three test conditions (EPA 1986b). Three samples were taken for the semivolatile organic compounds and triplicate VOC samples were taken.

Both EPA Method 0010 and 0030 sampling trains were prepared, set up at the sampling location, and analyzed to identify possible contamination.

Modified CARB Method 501
Particle size distributions were also measured using an in-stack cascade impactor. An Anderson® impactor was used in a modified California Air Resources Board (CARB) Method 501 (CARB 1990). This method allows size-segregated samples to be collected for determining either the relative mass fractions in each size range or the concentration of trace elements in each size range. These tests modified the CARB method slightly to allow for use in the research combustor. The CARB method places the impactor precutter in the stack. However, the PBS stack is too small to allow in situ placement of the impactor, so a buttonhook nozzle is used rather than the straight nozzle specified in the CARB method. Fewer runs are conducted during research testing than are called for in the CARB method, with only three runs used during research testing rather than the seven runs specified by the CARB method.

A blank CARB 501 impactor was also prepared and set up at the sampling location, and its filters subsequently weighed, to evaluate any contamination of the filters during the sampling procedures.

Chapter 5
EPA Pilot-Scale Test Results

Tests measuring air pollutant emissions were conducted on EPA's Package Boiler Simulator during May and June 1999. The tests measured emissions from the combustion of Orimulsion 100, Orimulsion 400, and a No. 6 fuel oil. Samples of Orimulsion 100 and Orimulsion 400 were obtained from Bitor America for the test program, and were shipped from Venezuela as part of normal shipments to the Dalhousie Generating Station in New Brunswick, Canada.

Test Conditions
To the extent possible, the tests followed the test matrix in Table 4-1. Actual operating conditions varied from the nominal test conditions in two ways. First, the O_2 levels specified in Table 4-1 were difficult to maintain. Second, the fuel feed system illustrated in Figure 4-2 required modification before either formulation of Orimulsion could be fed into the PBS over a period required for testing. These two problems are discussed in more detail below, and in Chapter 10 (Quality Assurance).

Fuel Composition
The composition of the fuel is important for several reasons. First, the fuel energy content will determine the fuel flow rate required to achieve a given load. Second, the sulfur content of the fuel will largely determine the SO_2 concentration. Third, the fuel nitrogen content can have a significant impact on NO_x formation. And finally, the trace metal content of the fuel will strongly influence the flue gas concentrations of those metals. Table 5-1 presents the analyses of the three fuels (No. 6 fuel oil, Orimulsion 100, and Orimulsion 400) supplied to EPA for these tests. Samples were taken from the fuel drums prior to testing.

O_2
Maintaining steady levels of O_2 at the nominal 3% specified in the test matrix was very difficult, if not impossible, for the duration of each test run. The PBS was influenced by changes in the stack draft level and by variations in air flow thought to be due to changes in the atomizing air pressure. Stack draft level is an issue for this unit because it is connected to the air pollution control system (APCS) along with several other test combustors. The APCS requires control of the inlet pressure, and therefore strongly influences the stack draft level of the PBS. Due to leaks in the PBS, changes in stack draft result in changes in the measured stack O_2 level independent of the inlet air flow. Combustion air flow settings were based both on theoretically determined levels as well as stack O_2 measurements to provide a degree of confidence that the O_2 level at the burner was adequate. However, considerable variability in stack O_2 levels remained. There appeared to be continuous fluctuations in atomizing air pressure, probably due to fluctuations in the air compressor (see Figures 4-2 and 4-3). Nevertheless, the flame appeared to maintain good stability and was not observed to fluctuate or generate significant levels of unburned fuel droplets for any of the three fuels. Several days of operation provided adequate confidence that the unit was operating well enough to allow testing to proceed, even though the stack O_2 levels varied more than desirable.

O_2 levels typically remained below 5%, except for several instances where recorded values exceeded 20% during CEM system failures. Values recorded during such excursions were not included in calculations of run or condition averages. Average values for the 12 test runs ranged between 2.3 and 4.6%. O_2 levels at the burner are believed to be slightly lower than these averages due to leakage of air into the PBS. Table 5-2 presents the average O_2 concentration for each test run and the average of the four test runs per condition. Plots of the CEM measurements are also presented in Appendix B for each test run.

Fuel Feed
Initial operation of the PBS and the fuel feed system shown in Figure 4-2 indicated that Orimulsion 100 could be fed through the same system used for heavy fuel oil, despite concerns over excessive shear rates (See Chapter 2). However, these initial operating periods were too short in duration to

Table 5-1. Elemental analyses (as received) of the three fuels tested.

	No. 6 Fuel Oil	Orimulsion 100	Orimulsion 400
Water, %	0.7	23.32	28.92
Carbon, %	86.45	64.20	58.12
Hydrogen, %	10.23	8.13	7.14
Nitrogen, %	0.26	0.25	0.17
Sulfur, %	2.07	3.05	2.23
Ash, %	0.08	0.17	0.07
Oxygen, % (by difference)	0.90	0.88	3.35
Antimony, µg/g	0.78	0.57	0.35
Arsenic, µg/g	2.6	2.9	2.2
Beryllium, µg/g	<0.005	<0.005	<0.005
Cadmium, µg/g	<0.005	<0.005	<0.005
Chromium, µg/g	0.58	0.235	0.20
Copper, µg/g	0.76	<0.005	<0.005
Iron, µg/g	51	12	22
Lead, µg/g	1.8	1.9	1.4
Magnesium, µg/g	7.6	342	1
Mercury, µg/g	<0.005	<0.005	<0.005
Nickel, µg/g	47	69	59
Selenium, µg/g	0.13	2.9	0.04
Vanadium, µg/g	221	324	262
Zinc, µg/g	8.9	0.90	0.37
Energy content, Btu/lb	18,121	13,919	12,596

Table 5-2. Average O_2 stack concentrations for each test run, and average of four test runs, in percent. Values in parentheses indicate standard deviation for each test run.

Fuel	Run 1	Run 2	Run 3	Run 4	Average
Orimulsion 100	2.74% (0.31)	2.62% (0.73)	3.47% (0.90)	2.57% (0.43)	2.85% (0.42)[1]
Orimulsion 400	3.96% (0.58)	3.40% (0.20)	2.33% (0.54)	4.37% (0.62)	3.51% (0.89)
No. 6 Fuel Oil	4.63% (0.52)	2.49% (0.77)	3.88% (0.78)	2.42% (0.45)	3.36% (1.08)

1. Standard deviation values for the condition averages are calculated using the four individual run average concentrations.

result in degradation of the Orimulsion, and subsequent operation for longer periods resulted in clogging of the fuel lines with bitumen that had separated from the water and in unstable and poor quality flames. The fuel feed system was modified as described in the previous chapter, and this resulted in much improved operation as well as elimination of the fuel degradation.

Some drift in the fuel flow rate remained, however, although incorporation of an additional pressure regulator in the fuel line minimized changes during individual test runs. Some variability in fuel flow remained, resulting in slightly different load levels from one test run to another. These changes were slight, however, and were not likely to have significantly influenced the measured emissions. Table 5-3 presents the fuel flows measured during each test run and the average fuel flow for each test condition.

Calculated load of the PBS during the test runs, based on fuel heat content and measured fuel flow, was on average, 1,037,000 Btu/hr with Orimulsion 100, 968,000 Btu/hr with Orimulsion 400, and 915,000 Btu/hr with No. 6 fuel oil.

Emission Measurement Results
CO
Average CO emissions were between approximately 15 and 40 ppm (corrected to 3% O_2) for all runs. The average CO emissions for No. 6 fuel oil were slightly lower than for either Orimulsion, but as Figure 5-1 shows, CO emissions were measured at below 20 ppm for at least one test run for both Orimulsion formulations. As noted above, CO emissions are strongly dependent upon O_2 level, and much of the variation in CO may be due to changes in O_2 levels during the test runs. Average O_2 levels for the three conditions were 2.8% for Orimulsion 100, 3.5% for Orimulsion 400, and 3.4% for No. 6 fuel oil. The Orimulsion tests also showed higher variability in both O_2 and CO levels than did the No. 6 fuel oil tests. Much of this variation was believed to be due to more and larger changes in O_2 level during the Orimulsion test runs than were seen during the No. 6 fuel oil runs.

CO increased significantly for all three fuels as O_2 levels dropped below a certain level. Unfortunately, the variation in O_2 levels and the air leakage into the PBS noted above make it impossible to accurately determine the O_2 level at which CO concentrations begin to increase. CO concentrations typically stayed below 50 ppm until O_2 dropped below a threshold value, then increased rapidly to greater than 1000 ppm. The threshold value differed for different test runs, and sometimes within a test run. For Orimulsion 100, the threshold O_2 value ranged from approximately 1.1 to 2.5% and for Orimulsion 400, the threshold value ranged from 1.8 to 3.5%. For No. 6 fuel oil, the threshold O_2 level ranged from 0.6 to 2.4%. Figure 5-2 plots CO against O_2 for each of the test runs.

CO concentrations also increased to relatively high levels for short periods during testing. These short-duration spikes occurred at apparently random intervals, and were believed to be caused by variations in fuel and air flows resulting in transient periods of low excess air. The relatively small

Table 5-3. Average fuel flows for each test run, and average of four test runs. Values in parentheses indicate standard deviation for each test run.

Fuel	Run 1	Run 2	Run 3	Run 4	Average
Orimulsion 100	0.1396 gpm (0.0364)	0.1418 gpm (0.0652)	0.1526 gpm (0.0199)	0.1540 gpm (0.0559)	0.1470 gpm (0.0736)[1]
Orimulsion 400	0.1426 gpm (0.0633)	0.1520 gpm (0.0460)	0.1641 gpm (0.0678)	0.1513 gpm (0.0781)	0.1525 gpm (0.0882)
No. 6 Fuel Oil	0.1013 gpm (0.0416)	0.1006 gpm (0.0332)	0.1035 gpm (0.0299)	0.0972 gpm (0.0440)	0.1006 gpm (0.0264)

1. Standard deviation values for the condition averages are calculated using the four individual run average concentrations.
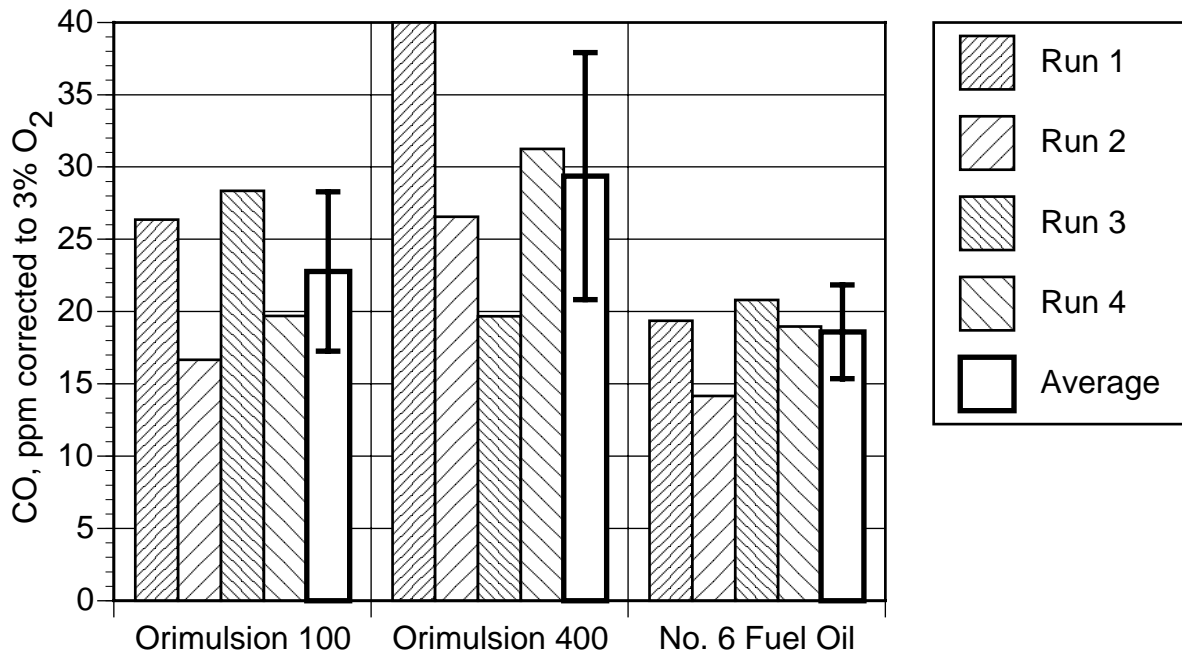
Figure 5-1. Average CO emissions from the three fuels tested in ppm, corrected to 3% O_2. Average values for each of the 12 test runs and average for each condition are shown.
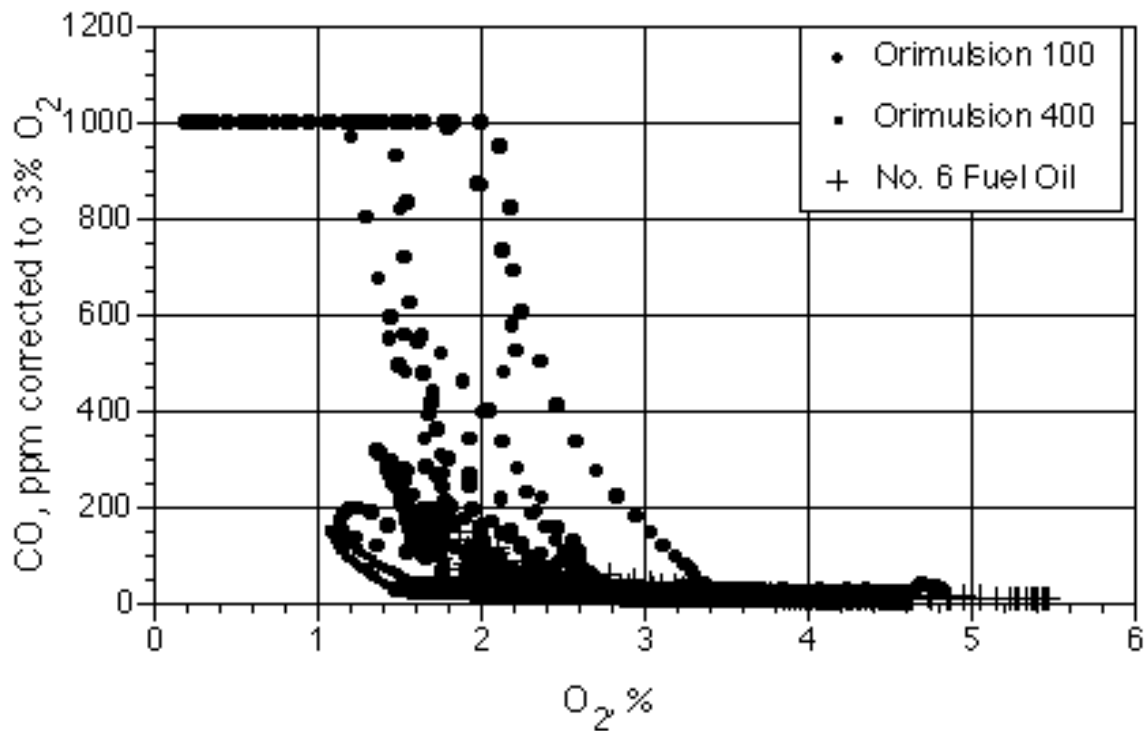
Figure 5-2. CO vs. O_2 for selected runs with Orimulsion 100, Orimulsion 400, and No. 6 fuel oil.
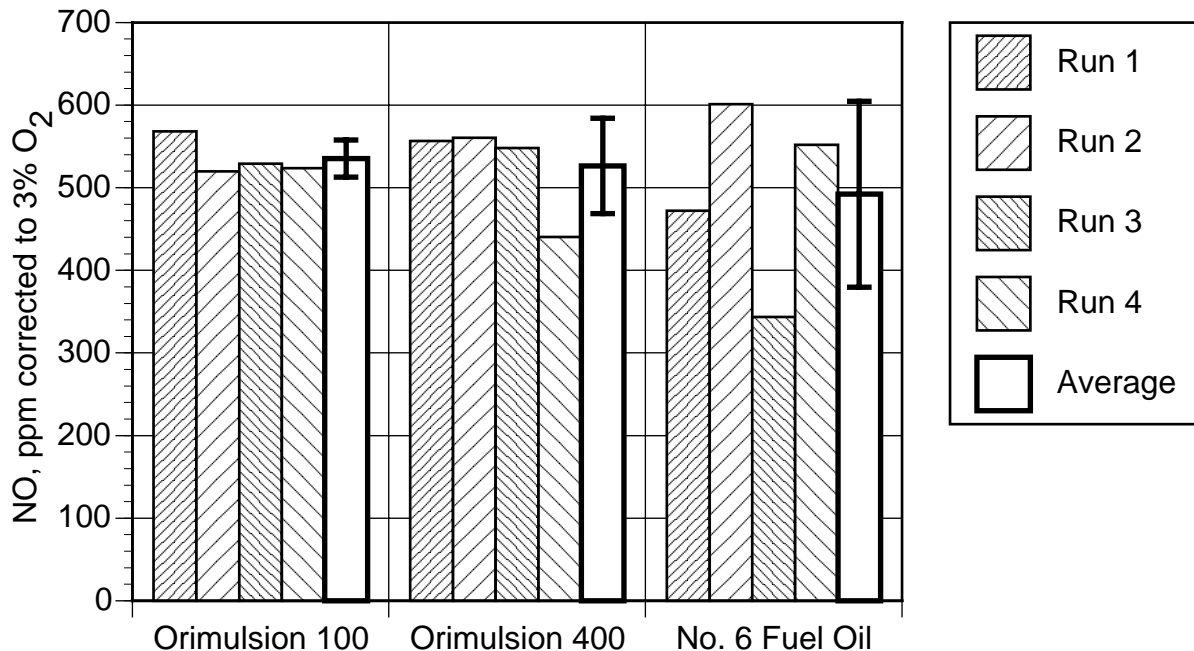
Figure 5-3. Average NO emissions from the three fuels tested in ppm, corrected to 3% O_2. Average values for each of the 12 test runs and average for each condition are shown. Error bars represent 1 standard deviation about the average.

size of the combustor makes this unit more sensitive to small fluctuations in fuel and air flows than would be seen in a full-scale unit.

NO_x

Only concentrations of nitric oxide (NO) were measured during EPA's pilot-scale testing. NO emissions averaged near 500 ppm (corrected to 3% O_2) for each of the three fuels. Here, the NO values were much steadier across test runs for Orimulsion 100 and Orimulsion 400 than for No. 6 fuel oil. Given the range of uncertainty in the average values (indicated by the ±1 standard deviation error bars in Figure 5-3), it is not possible to discern any significant difference in NO emission levels between the three fuels. There was a slight drop in NO with decreasing stack O_2, similar to what one would observe from other hydrocarbon fuels. Figure 5-4 shows typical levels of NO concentrations for the range of O_2 levels in the PBS.

SO_2 and SO_3

Likewise, average SO_2 emissions as measured using CEMs (presented in Figure 5-5) were found to be essentially the same for each of the three fuels, at 1000 ppm (corrected to 3% O_2). Although the average SO_2 measurement for the No. 6 fuel oil is slightly lower than either of the Orimulsion formulations, the measured variability in the average value for the fuel oil makes it impossible to state that there is any significant difference between SO_2 emissions from the No. 6 fuel oil used in these tests and either of the two Orimulsion formulations.

Using the MACS sampling train, SO_2 concentrations were measured at 1220 ppm for the No. 6 fuel oil, 1640 ppm for Orimulsion 100, and 2010 ppm for Orimulsion 400. Based on the analyses of the fuels' sulfur contents, if 100% of the sulfur were to be emitted as SO_2, one would expect SO_2 concentrations to be roughly 1000 ppm for the No. 6 fuel oil, 2400 ppm for Orimulsion 100, and 1800 ppm for Orimulsion 400. These values, as well as the CEM measurements, are presented in Table 5-4.
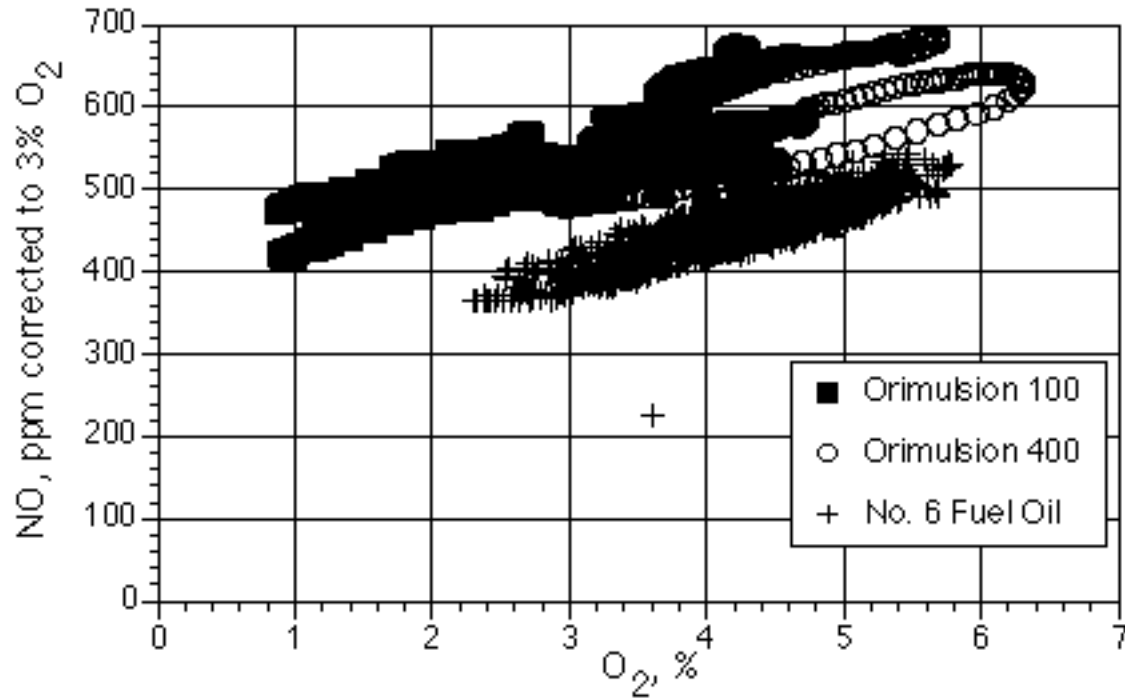
Figure 5-4. NO vs. O_2 for selected runs with Orimulsion 100, Orimulsion 400, and No. 6 fuel oil.
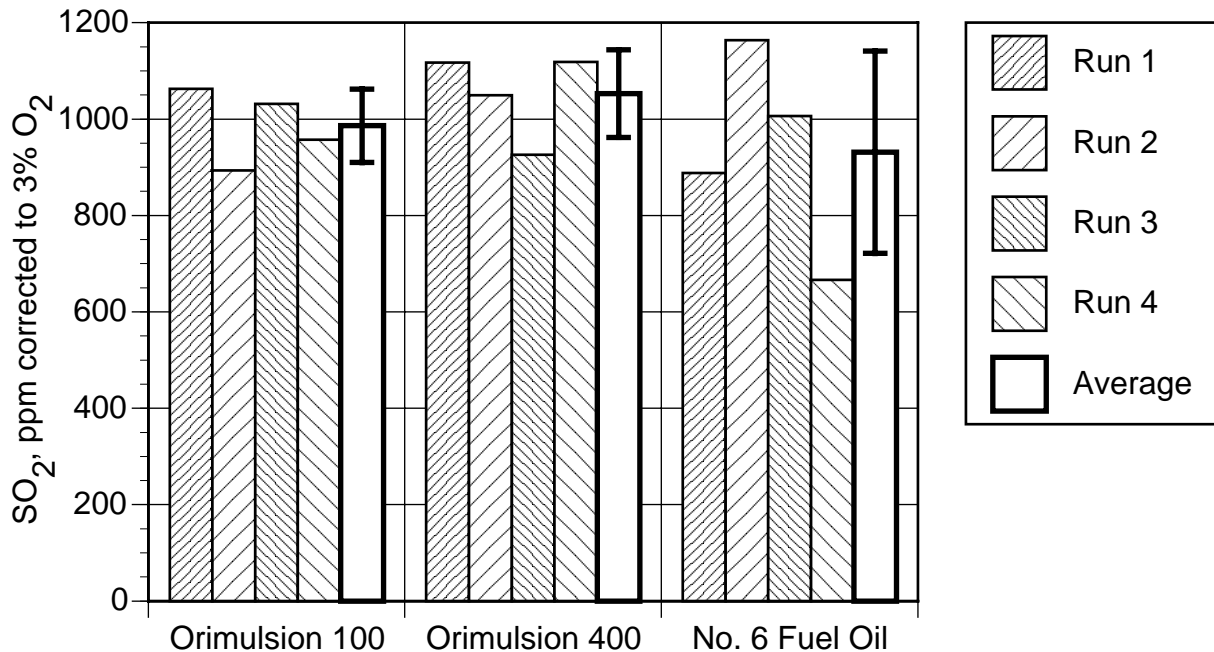
Figure 5-5. Average SO_2 emissions as measured by CEM from the three fuels tested in ppm, corrected to 3% O_2. Average values for each of the 12 test runs and average for each condition are shown. Error bars represent 1 standard deviation about the average.

While the CEM measurements are consistently lower than the MACS measurements, the differences are not consistent across the fuels. Neither measurement method is consistently higher or lower than

the corresponding calculated value.

It is unclear why these discrepancies exist. One hypothesis is that the "missing" sulfur (the differences between the calculated concentrations and the concentrations measured by CEMs) is due to SO_3 formation. However, this would result in SO_3 concentrations between 800 and 1400 ppm for the two Orimulsion formulations, which would be substantially higher than anything reported in the literature or than what would be expected based on the properties of the fuel. While these values are slightly higher than the SO_2 concentrations measured by CEMs, SO_3 concentrations that are roughly equivalent to SO_2 concentrations are not unreasonable. Although the MACS system measured SO_3 concentrations of only 1 ppm on two occasions, these measurements are difficult to take correctly, and may be the source of the error.

A second hypothesis is that the fuel analyses were incorrect. This could account for the differences between the measured and calculated SO_2 concentrations, but not for the differences between the two measurement methods. A third hypothesis is that the measurements were incorrect. While this could explain the discrepancies, both the CEM and the MACS results would have to be in error for this to explain the differences. The CEMs were calibrated before and after each test run, providing some indication of CEM data reliability (see Chapter 10 for further discussion of calibration procedures). There were no indications of problems to such a degree that would satisfactorily explain the difference between CEM and calculated SO_2 concentrations.

A fourth possible reason for lower measured SO_2 concentrations could be a reaction with the Mg additives on the filter of the sampling equipment. Mg additives were not used during testing of the No. 6 fuel oil, but were used (in different forms) for both Orimulsion formulations.

A comparison of data from full-scale plants reported in Chapter 3 shows that uncontrolled SO_2 concentrations ranged between 2200 and 2400 ppm when burning Orimulsion 100. This is consistent with the calculated value for Orimulsion 100 in Table 5-4. Given the consistency between CEM and calculated SO_2 concentrations for the No. 6 fuel oil, it is reasonable to conclude that the CEM measurements reported for these pilot-scale tests are probably low, particularly for the Orimulsion tests. There may have been some interference between flue gas components and the CEM's SO_2 measurements during the Orimulsion tests, although there have been no indications of such interferences discussed in the literature.

The available evidence does not suggest that the differences in SO_2 concentrations for the No. 6 fuel oil and the two Orimulsion formulations are due to differences in the fuels other than sulfur content. Full-scale results and understanding of combustion behavior would indicate that uncontrolled SO_2 concentrations from Orimulsion will in practice be quite close to the calculated values based on fuel sulfur content.

PM

PM emissions do show some differences between the three fuels (see Figure 5-6). The Orimulsion 400 and No. 6 fuel oil had PM concentrations that were approximately 25% lower (at 150 mg/Nm[3]) than those from Orimulsion 100 at approximately 200 mg/Nm[3]. The analysis of Orimulsion 100 showed both higher ash levels and higher amounts of magnesium than were present for either of the other two fuels. These differences are likely to have accounted for the difference in PM

Table 5-4. SO_2 concentrations for the three fuels tested as measured by CEM and MACS methods, and as calculated based on complete conversion of fuel sulfur to SO_2.

	CEM Measurements	MACS Measurements	Calculated Concentrations
No. 6 Fuel Oil	910	1220	960
Orimulsion 100	990	1640	2400
Orimulsion 400	1020	2010	1820

concentrations between the three fuels. Loss on ignition (LOI) values were determined for PM samples from each of the fuels. The samples were collected on the large dilution sampler filter, downstream of a cyclone designed to remove particles larger than 2.5 μm in diameter. Of the three fuels, only the No. 6 fuel oil had any measurable amount of mass in the cyclone catch. The cyclone catch and samples of the large filters for each fuel were subject to LOI analyses. The filters all indicated no measurable LOI (above that measured for a blank filter), and the No. 6 fuel oil cyclone catch had an LOI value of 59%. The high LOI measurement is not unexpected, as the larger particles in the No. 6 fuel oil sample are likely to be largely unburned carbon.

Particle size distributions show a marked difference between Orimulsion and the No. 6 fuel oil. The fraction of total particle mass collected on an Andersen cascade impactor is plotted versus particle size for the three fuels in Figure 5-7. Approximately 80% of the total particle mass captured was smaller than 1 μm in diameter for both Orimulsion 100 and Orimulsion 400, compared to 50% of the particle mass for the No. 6 fuel oil. Approximately 90% of the particle mass was smaller than 2.5 μm in diameter for both Orimulsion formulations, compared with approximately 75% for the No. 6 fuel oil. All three fuels have a bimodal particle size distribution to at least a slight degree, with Orimulsion 400 and the No. 6 fuel oil showing a larger coarse (particles > 6 μm in diameter) mode than the Orimulsion 100. The coarse mode is likely to be due to incomplete combustion of the bitumen droplets in the case of Orimulsion and of the fuel spray droplets in the case of the No. 6 fuel oil.

Results from the scanning mobility particle sizing system (SMPS) provide more detail regarding the particle size distributions for particles smaller than 1 μm in diameter, as shown in Figure 5-8. Even in this size range, there are differences in the size distributions. The Orimulsion 400 and No. 6 fuel oil are quite similar, with modes between 0.06 and 0.08 μm, while the Orimulsion 100 has a smaller mode at just larger than 0.1 μm. The SMPS measurements for the No. 6 fuel oil show a slight indication of the mode near 1 μm, as $dV/d(\log D_p)$ begins to curve upward for particles larger than about 0.3 μm.
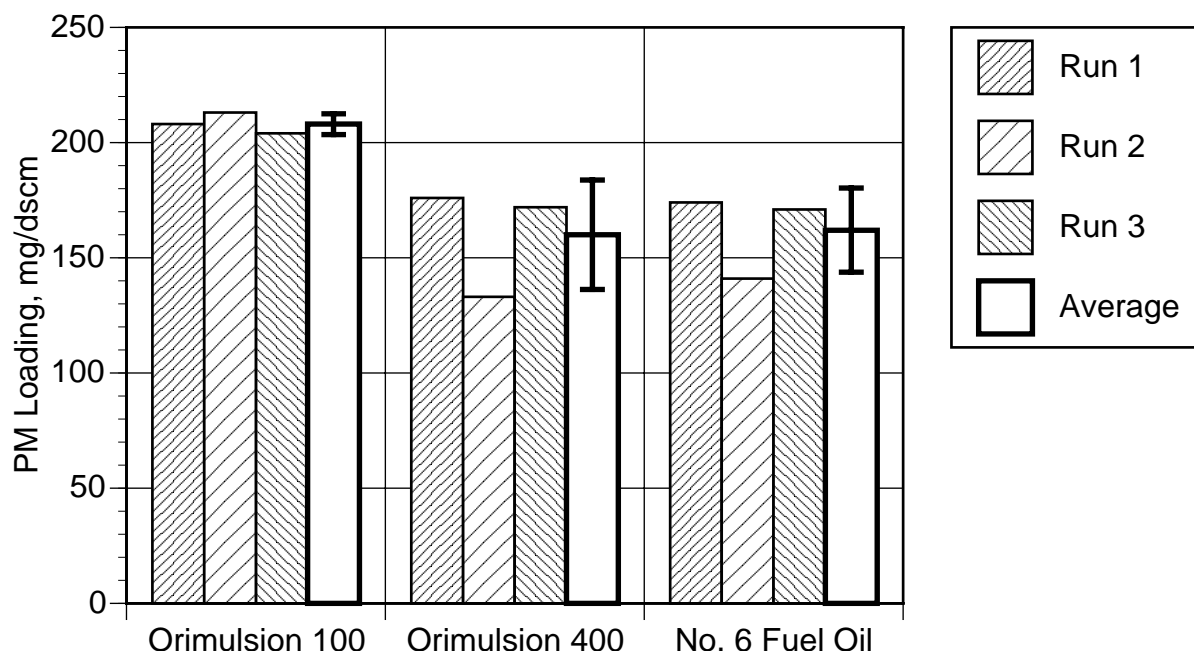
Figure 5-6. Average PM emissions in mg/dscm from the three fuels tested. Average values for each of the 12 test runs and average for each condition are shown. Error bars represent 1 standard deviation about the average.
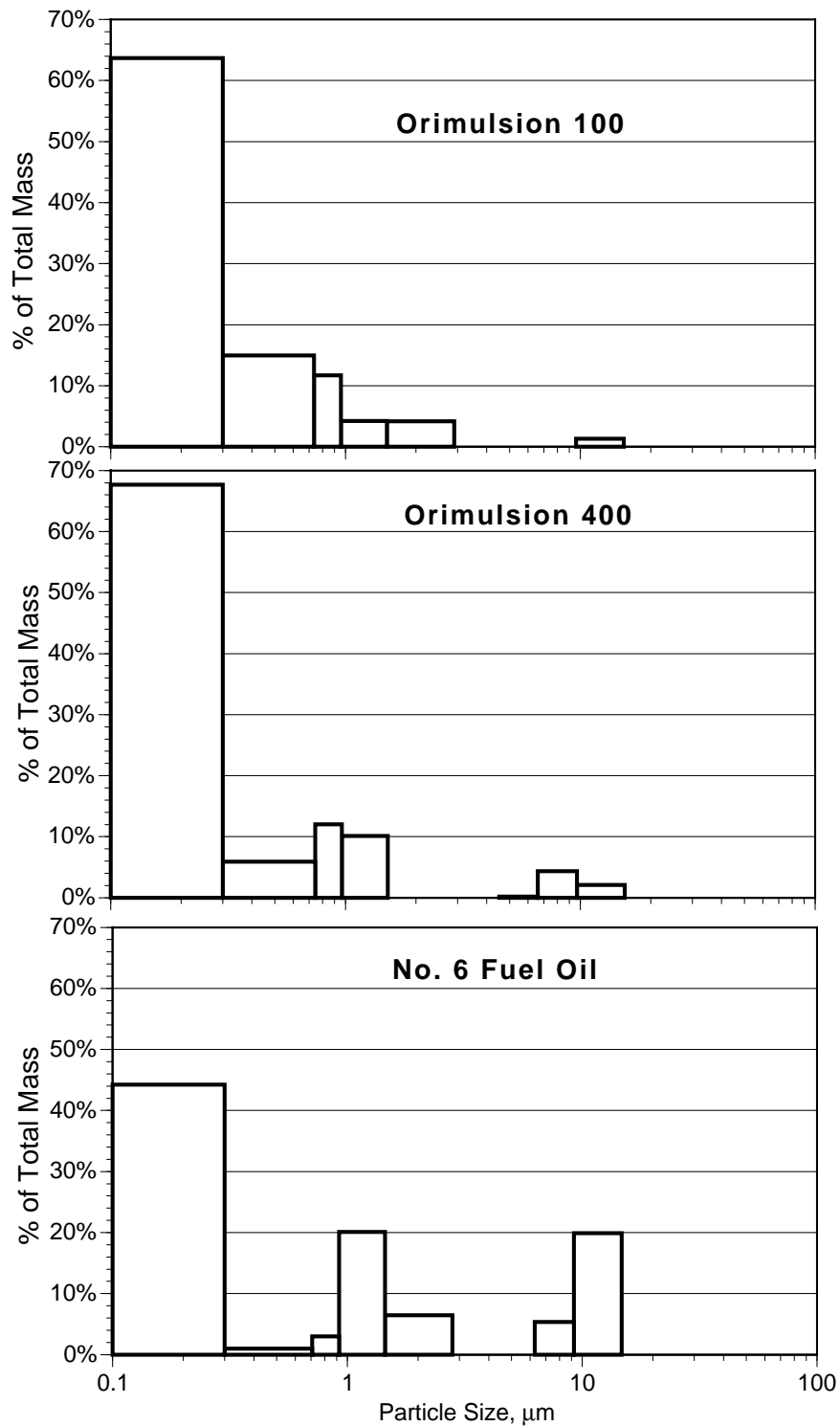
Figure 5-7. Cascade impactor results for the three fuels tested.

The SMPS data reflect volume distributions and the cascade impactor data are mass distributions, making it necessary to transform volume distributions to mass distributions using size-specific

particle density. The difference between mass and volume may explain the similarity of particle size distributions for Orimulsion 400 and No. 6 fuel oil as measured by SMPS compared to the difference as measured by mass using the impactor.

Organic HAPs

Both volatile and semivolatile organic compounds were sampled during the test program. Each sample was analyzed for a total of 33 volatile organic compounds (VOCs) and 96 semivolatile organic compounds (SVOCs). Three samples were collected for each fuel. The compounds for which the samples were analyzed are given in Tables 5-5 (VOCs) and 5-6 (SVOCs).

Volatile Organic Compounds

In general, very low levels of VOCs were detected. Only 9 of the 33 VOCs were detected (the highest detection level for all the VOCs was 0.259 µg/dscm), with two of those compounds (iodomethane and dichloromethane) being present as laboratory contaminants. Of the remaining 7 VOCs, carbon disulfide, benzene, and toluene were detected in 9 of the 9 samples, m,p-xylenes and styrene were detected in 8 of the 9 samples (both compounds in 2 of 3 Orimulsion 100 samples and 3 of 3 of the other fuels), ethylbenzene was detected in 5 of 9 samples (in 1 of 3 samples of Orimulsion 100 and Orimulsion 400 and in 3 of 3 samples of No. 6 fuel oil), and o-xylenes were detected only in 3 of 3
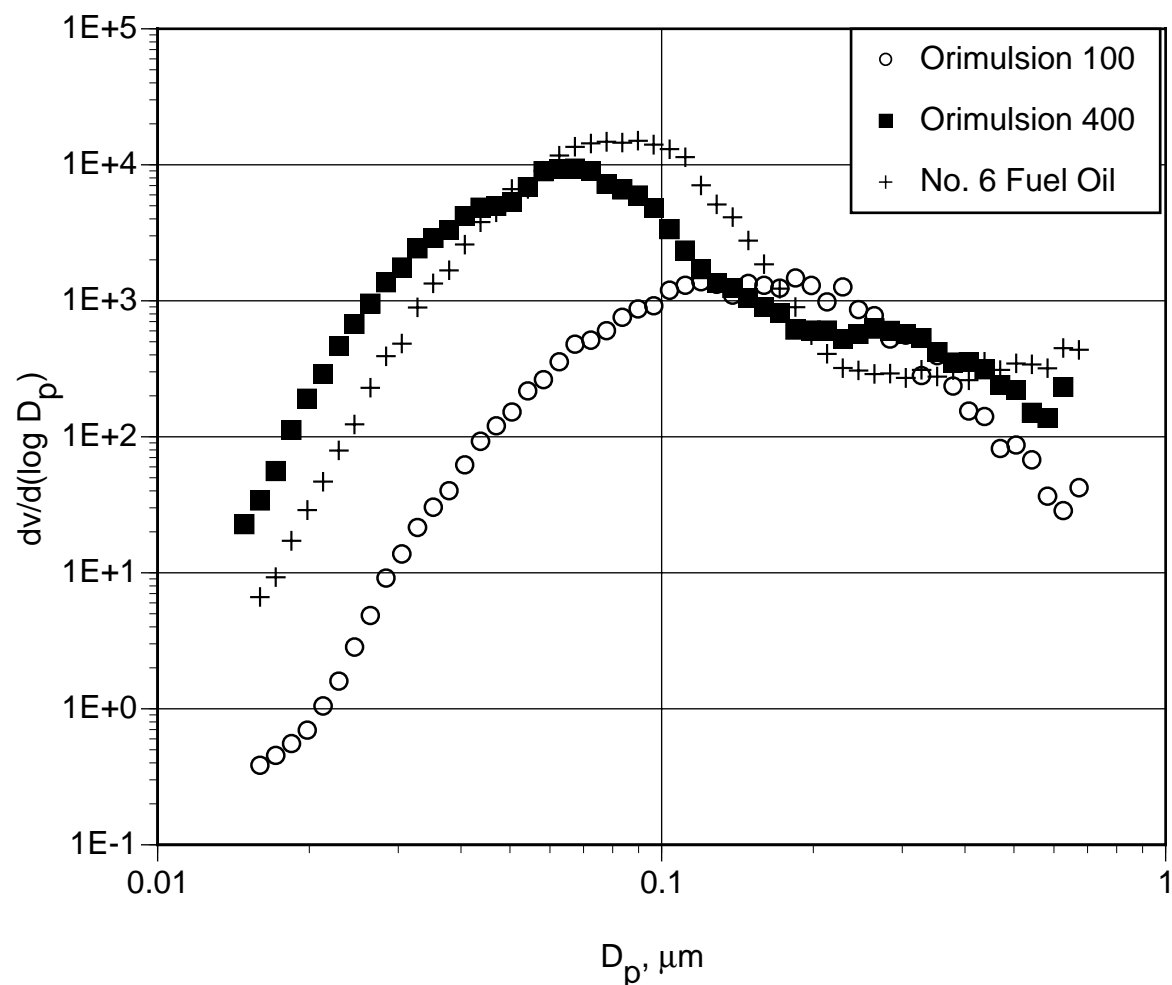
Figure 5-8. Scanning mobility particle sizing results for the three fuels tested.

Table 5-5. Volatile organic compounds for which samples were analyzed.

1,1 Dichloroethene	Carbon Tetrachloride
1,1,1-Trichloroethane	Chlorobenzene
1,1,2-Trichloroethane	Chloroform
1,1-Dichloroethane	Dibromochloromethane
1,2-Dibromoethane	Dibromomethane
1,2-Dichlorobenzene	Dichloromethane
1,2-Dichloroethane	Ethylbenzene
1,2-Dichloropropane	Iodomethane
1,3-Dichlorobenzene	m,p-Xylenes
1,4-Dichlorobenzene	o-Xylene
Benzene	Styrene
Bromobenzene	t-1,2-Dichloroethene
Bromochloromethane	t-1,3-Dichloropropene
Bromodichloromethane	Tetrachloroethene
c-1,2-Dichloroethane	Toluene
c-1,3-Dichloropropene	Trichloroethene
Carbon Disulfide	

No. 6 fuel oil samples. Figure 5-9 shows the average detected concentrations of the VOCs in the three fuels in μg/dscm, and Figure 5-10 presents the average emission factors of the 7 detected VOCs in lb/10^{12} Btu. Both average concentrations and average emission factors are calculated using only detected values, and do not use 0 or other value to reflect samples with concentrations below the detection limit. For m,p-xylenes, styrene, and ethylbenzene, the average concentrations of VOCs in Orimulsion 100 and Orimulsion 400 shown in Figure 5-9 are high, since incorporation of the method detection level or zero in the average would reduce the reported value. The concentrations of VOCs in No. 6 fuel oil flue gases would not be affected, since each of the 7 VOCs was detected in each of the 3 samples for No. 6 fuel oil.

There are no significant differences in VOC emissions between the three fuels, even if variability in measurements is not considered. The largest difference in concentrations of a particular compound between the three fuels was for benzene, with roughly 2.4 μg/dscm difference between Orimulsion 400 (at 3 μg/dscm) and No. 6 fuel oil (at 0.6 μg/dscm). This difference may be high on a percentage basis, but in absolute terms is very small. As an illustration, the annual mass emissions of benzene from a 500 MW power plant operating 24 hrs/day, 365 days/yr with a 10,000 Btu/kW-hr heat rate would result in 72 lb (32.8 kg) of benzene emissions when burning Orimulsion 400 if emissions were at the concentration measured in these tests. Each of the other compounds would be emitted at lower annual levels for either Orimulsion 400 or the other two fuels. These values can be calculated from the emission factors presented in Figure 5-10.

Semivolatile Organic Compounds
Flue gases from each of the three fuels were sampled and analyzed for 98 semivolatile organic compounds, including 16 polycyclic aromatic hydrocarbons (PAHs). Of these 98 compounds, only 9 semivolatile organic compounds were detected. Of these 9, 4 were phthalates, a common laboratory contaminant. The semivolatile organic compounds detected were 1,4-dichlorobenzene, 2-

Table 5-6. Semivolatile organic compounds for which samples were analyzed. PAHs are underlined.

1,2,4,5-Tetrachlorobenzene	2-Methylphenol	<u>Benzo(a)pyrene</u>	Hexachlorobutadiene
1,2,4-Trichlorobenzene	2-Naphthylamine	<u>Benzo(b)fluoranthene</u>	Hexachlorocyclopentadiene
1,2-Dichlorobenzene	2-Nitroaniline	<u>Benzo(ghi)perylene</u>	Hexachloroethane
1,3 Dinitrobenzene	2-Nitrophenol	<u>Benzo(k)fluoranthene</u>	Hexachloropropene
1,3,5-Trinitrobenzene	3,3'-Dichlorobenzidine	Benzyl Alcohol	<u>Indeno(1,2,3-cd)pyrene</u>
1,3-Dichlorobenzene	3,3'-Dimethylbenzidine	Benzyl butyl phthalate	Isodrin
1,4-Dichlorobenzene	3-Methylcholanthrene	Bis (2-chloroethyl) ether	Isophorone
1,4-Naphthoquinone	3-Nitroaniline	Bis(2-chloroethoxy)methane	Isosafrole
1-Naphthylamine	4-Aminobiphenyl	Bis(2-chloroisopropyl)ether	Methyl Methanesulfonate
1-Nitrosopiperidine	4-Bromophenyl phenyl ether	Chlorobenzilate	n-Nitrosodi-n-butylamine
2,3,4,6-Tetrachlorophenol	4-Chloro-3-methyl-phenol	<u>Chrysene</u>	N-nitrosodi-n-propylamine
2,4,5-Trichlorophenol	4-Chloroaniline	Di-n-butyl phthalate	n-Nitrosodiethylamine
2,4,6-Trichlorophenol	4-Chlorophenyl phenyl ether	di-n-octyl phthalate	n-Nitrosomethylethylamine
2,4-Dichlorophenol	4-Methylphenol	Diallate	n-Nitrosospyrrolidine
2,4-Dimethylphenol	4-Nitroaniline	<u>Dibenz(a,h)anthracene</u>	<u>Naphthalene</u>
2,4-Dinitrophenol	4-Nitrophenol	Dibenzofuran	Nitrobenzene
2,4-Dinitrotoluene	5-Nitro-o-toluidine	Diethyl phthalate	p-Dimethylaminoazobenzene
2,6-Dichlorophenol	7,12-Dimethylbenz(a)anthracene	Dimethyl phthalate	Pentachlorobenzene
2,6-Dinitrotoluene	<u>Acenaphthene</u>	Dinoseb	Pentachloronitrobenzene
2-Acetylaminofluorene	<u>Acenaphthylene</u>	Diphenylamine	Pentachlorophenol
2-Chloronaphthalene	Acetophenone	Ethyl methanesulfonate	Phenacetin
2-Chlorophenol	Aniline	<u>Fluoranthene</u>	<u>Phenanthrene</u>
2-Methyl-4,6-dinitrophenol	<u>Anthracene</u>	<u>Fluorene</u>	Phenol
2-Methylnaphthalene	<u>Benzo(a)anthracene</u>	Hexachlorobenzene	<u>Pyrene</u>

methylnaphthalene, acetophenone, benzyl butyl phthalate, di-n-butyl phthalate, di-n-octyl phthalate, diethyl phthalate, naphthalene, and phenol.

The semivolatile organic compound analysis method (Method 8270) analyzes the sampling train condensate, the filter, and the XAD resin for presence of the compounds. Thus there are 3 samples to be analyzed for each test run. Since each fuel was sampled 3 times, a total of 9 samples were analyzed for each fuel. Table 5-7 shows the semivolatile compounds with concentrations measured above the detection level of 1 μg in the analyte (corresponding to a maximum flue gas detection level of 0.47 μg/dscm), and the number of times each compound was detected in the 9 samples per fuel. None of the 9 compounds were detected in all samples, and 2 compounds (1-4 dichlorobenzene and 2 methylnaphthalene) were detected in only 1 sample of the No. 6 fuel oil. Benzyl butyl phthalate was not detected in any of the No. 6 fuel oil samples, in only 1 of the Orimulsion 100 samples, and 2 of the Orimulsion 400 samples. The remaining semivolatile organic compounds were detected in

each of the three fuels, with samples registering detection ranging from 1 of 9 (naphthalene in Orimulsion 100) to 7 of 9 (di-n-octyl phthalate in No. 6 fuel oil). The number of times detected gives an indication of the likelihood of measuring these compounds as existing in the flue gases, as opposed to being laboratory contaminants. The more samples a compound is detected in, the more likely it is to be present in the flue gas and not simply a laboratory contaminant.

The concentrations of semivolatile organic compounds in the flue gases of the three fuels were relatively low. The compound with the minimum concentration detected in all three fuels was naphthalene, at a level of just over 2 µg/dscm in Orimulsion 400 flue gases (see Figure 5-11). The highest concentration of the semivolatile organic compounds was the 9.3 µg/dscm of di-n-butyl phthalate measured in No. 6 fuel oil flue gases. Emission rates in lb/10^{12} Btu are presented in Figure 5-12 for the three fuels. Using the same scenario as for the VOCs, the maximum annual mass emissions would be of di-n-butyl phthalate, at about 680 lb/yr. Total mass emissions of PAHs in this scenario would be 92 lb/yr (assuming the nondetect values were zero). Differences in semivolatile organic compound emissions between the three fuels are slight. Measurement variability (not shown in Figure 5-12) was high for these measurements, making it difficult to determine any significant differences.
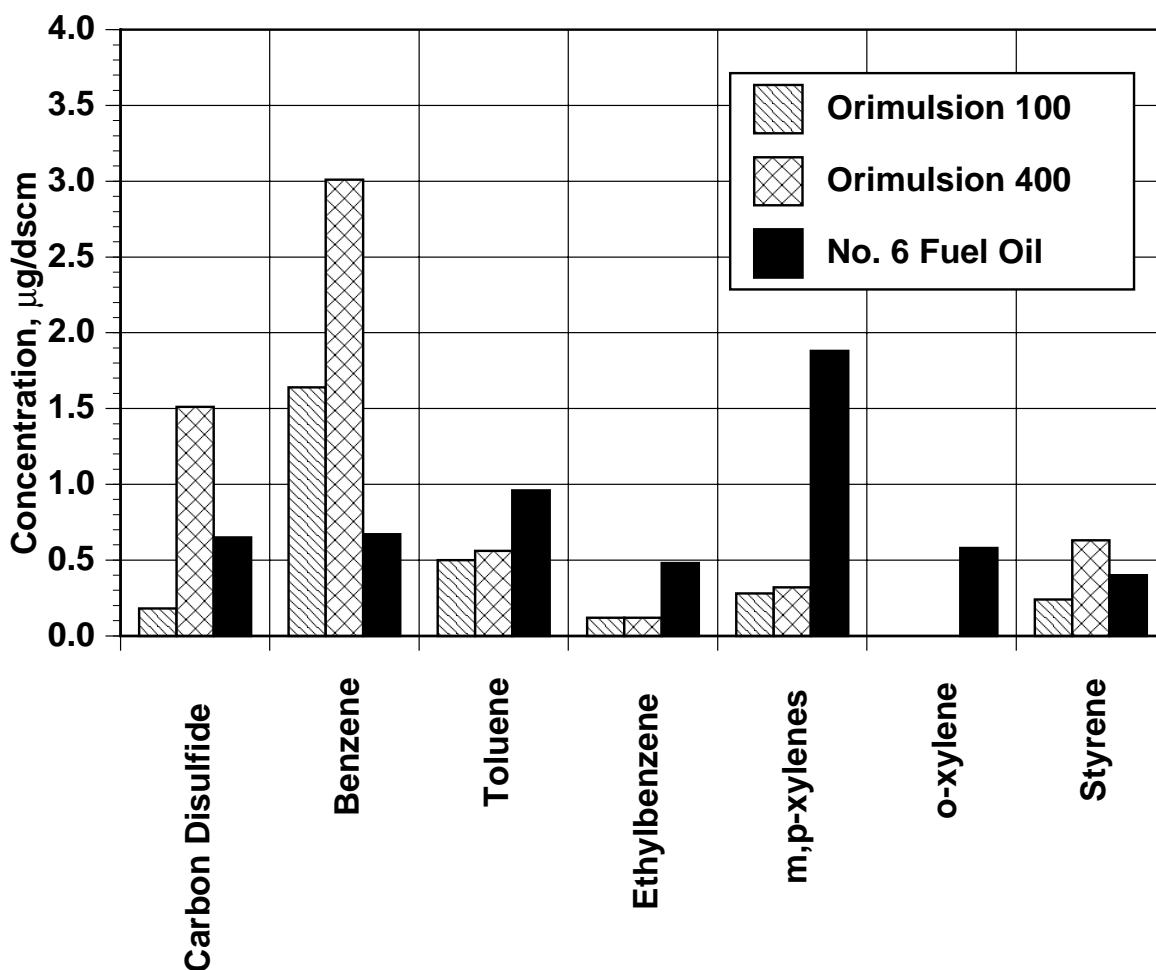
Figure 5-9. Average detected concentration of volatile organic compounds in the flue gases of the three fuels tested. Concentration values for ethylbenzene, m,p-xylenes, and styrene do not reflect the samples for which these compounds were not detected in Orimulsion 100 and Orimulsion 400 flue gases.

Metals

The concentration of metals in the flue gases from the three fuels are shown in Figure 5-13. This figure is divided into 3 sections to better show the differences in metal concentrations. Each sample was analyzed for 12 metals: Sb, As, Be, Cd, Cr, Cu, Fe, Mg, Mn, Ni, V, and Zn. Each metal was detected in each sample, except for Sb, which was detected only in the No. 6 fuel oil. Sb, As, Be, Cd, Cr, and Mn were each measured at concentrations near 10 μg/dscm, with minor differences between the fuels.

In several instances, the percent recovery of several metals was relatively poor. Recovery is defined here as the percent of metal mass emissions measured in the flue gas divided by the metal mass emissions calculated based on the amount of metal in the fuel. Table 5-8 presents the percent recovery for each of the metals for which analysis was conducted in these tests. Recovery values over 100% indicate that more metal was measured in the stack than would have been expected, based on 100% emissions of that metal in the fuel. Recoveries below 100% indicate that less metal was emitted in the stack gases than would have been expected, based on 100% of that metal in the fuel being emitted.

Recoveries for the two major metals of concern from Orimulsion and heavy fuel oil, Ni and V, were near 100%. Recoveries ranged from just under 80% to just over 102%, with an average for all the fuels being 94.2%. Recoveries for Be and Cd were on the order of 1000% for each of the three fuels. Both of these metals were not found in any of the three fuels, and the values used to calculate a maximum emission factor were the fuel analysis detection limits. It is likely that the detection levels
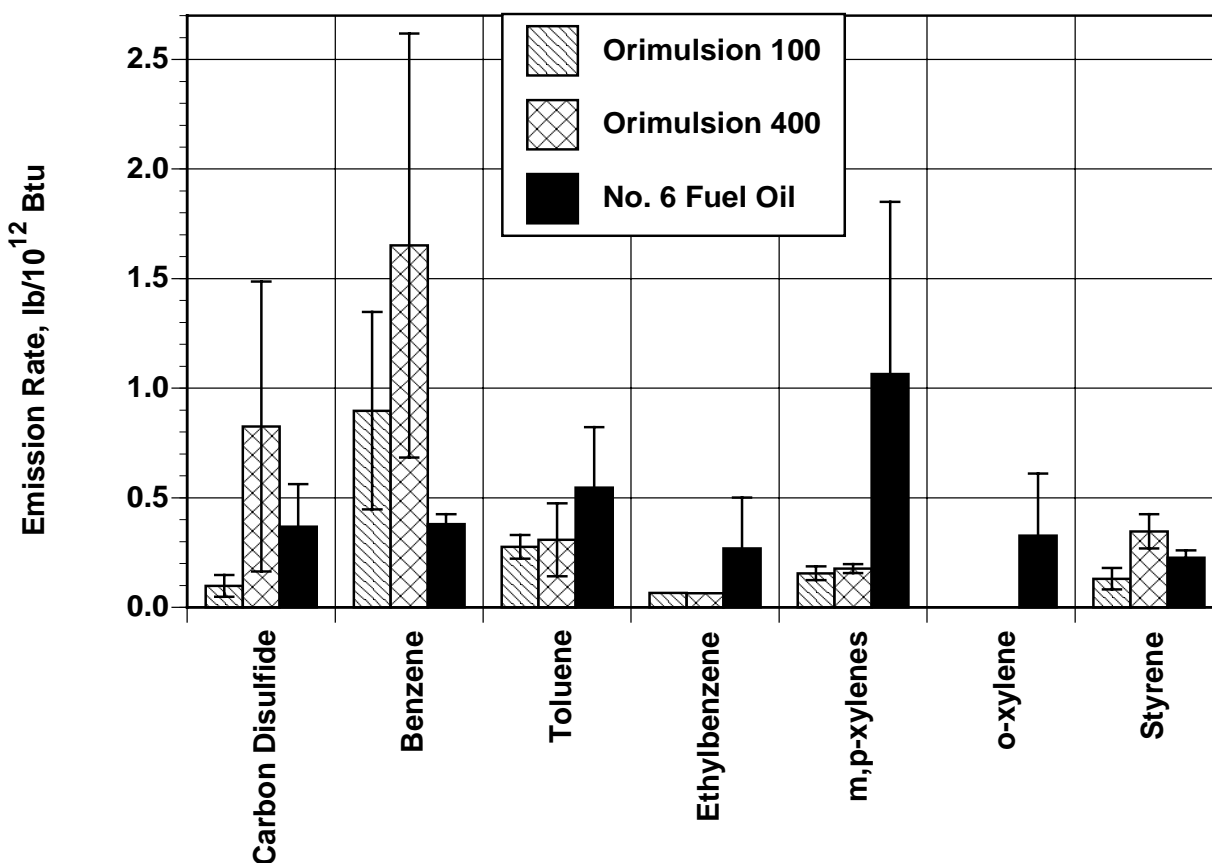
Figure 5-10. Average detected emission factors of volatile organic compounds in the flue gases of the three fuels tested. Emission factor values for ethylbenzene, m,p-xylenes, and styrene do not reflect the samples for which these compounds were not detected in Orimulsion 100 and Orimulsion 400 flue gases.

reported for the fuel analyses were somewhat low, resulting in calculated emission factors that were well below the value the method could in fact detect. Measured emission factors for both Be and Cd were quite low for all three fuels, with a maximum value of 8.45 lb/10^{12} Btu.

The results for Cu are similar to those for Be and Cd. Cu was not detected in either Orimulsion formulation, but was detected in the No. 6 fuel oil. Recoveries of Cu were again on the order of 1000% for the Orimulsion formulations, but were within a factor of 2 for the No. 6 fuel oil (59%). The other remaining recovery significantly greater than 100% was for Mg from Orimulsion 400. In this case, the fuel analysis did not account for the injection of $Mg(OH)_2$ into the fuel immediately prior to burning, and it was expected that the stack gas concentration of Mg would be substantially higher than would be predicted based on fuel content of Mg alone.

There were also several metals that exhibited very low recoveries, on the order of 1%. Arsenic (As) was measured at less than 2% of the levels that would be expected based on the As level in each of the three fuels. Sb was measured at less than 1% of the calculated level for Orimulsion 100 and Orimulsion 400, and at just over 22% for No. 6 fuel oil. Orimulsion 100 and Orimulsion 400 also showed very low recoveries for Fe, at less than 4% for both fuels, while over 45% of Fe was recovered from the No. 6 fuel oil. The low recovery of Fe from both Orimulsion formulations makes the differences in measured emissions shown in Figure 5-12 somewhat less severe, although the No. 6 fuel oil would still be the highest Fe emitter of the three if 100% of the Fe measured in the fuel were emitted through the stack. If 100% of Fe were recovered in the stack gases of all three fuels, each would emit on the order of 1000 lb/10^{12} Btu, rather than No. 6 fuel oil measured in 1000s and Orimulsion measured in 10s. Zn was also recovered at relatively low rates, particularly for Orimulsion 100. Again, the low recovery rates magnify the apparent differences between Orimulsion and the No. 6 fuel oil, although the No. 6 fuel oil would still emit roughly an order of magnitude more Zn than either of the Orimulsion formulations if 100% recovery were achieved. Mg recovery for Orimulsion 100 was also quite low, at only 3.3%.

Low recovery rates may reflect a buildup of deposits in the combustor. However, there was no indication of significant deposition in the PBS during or following the test campaign. Other reasons for low recovery include sampling, preparation, and analysis errors. While these problems are quite possible, the recovery of metals in samples spiked with known amounts of metals was quite good (see Chapter 11), and did not indicate widespread problems in sample collection, handling, or analysis.

Table 5-7. Semivolatile organic compounds detected in the flue gases of the three fuels and the number of times each compound was detected in the 9 samples collected for each fuel.

Compound	Number of Detects, Orimulsion 100	Number of Detects, Orimulsion 400	Number of Detects, No. 6 Fuel Oil
1-4 Dichlorobenzene	0	0	1
2 Methylnaphthalene	0	0	1
Acetophenone	3	3	3
Benzyl butyl phthalate	1	2	0
Di-n-butyl phthalate	6	5	6
Di-n-octyl phthalate	3	2	3
Diethyl phthalate	3	2	3
Naphthalene	1	2	2
Phenol	5	4	4
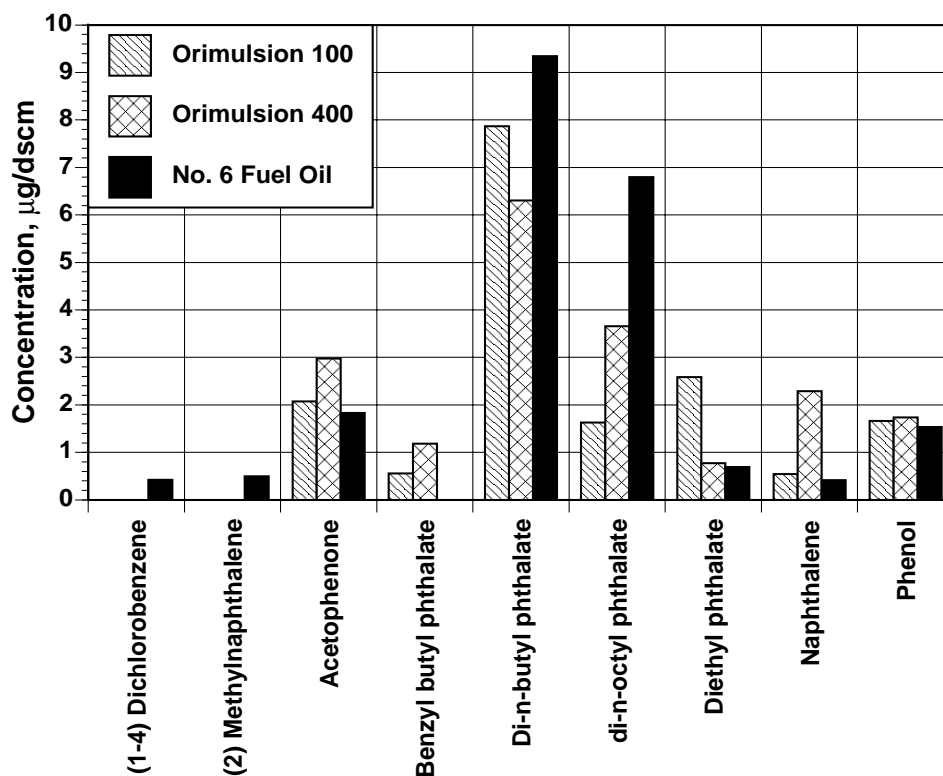
Figure 5-11. Average detected concentrations of semivolatile organic compounds in the flue gases of the three fuels tested.
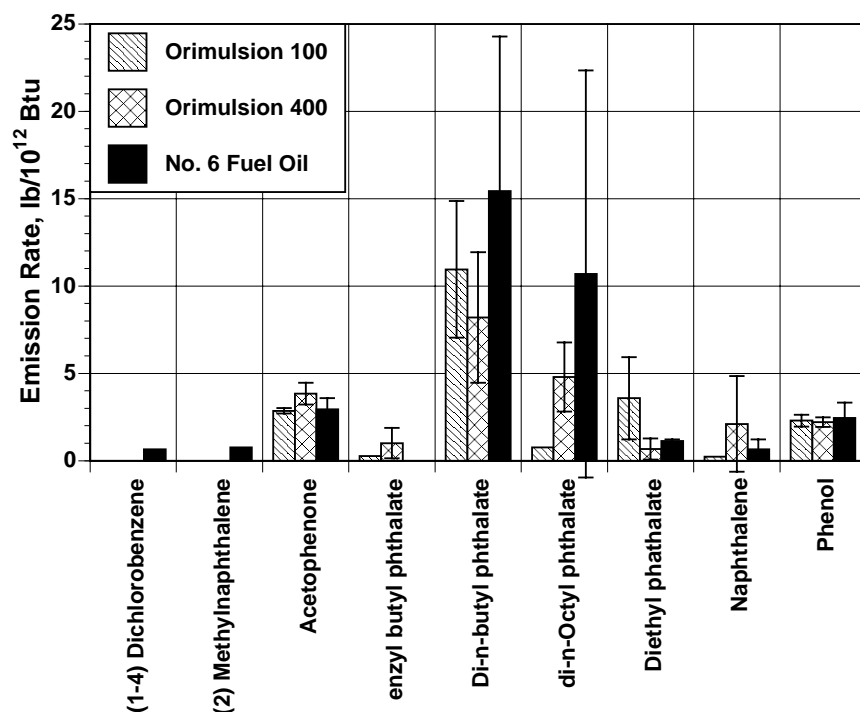
Figure 5-12. Average detected emission factors of semivolatile organic compounds in the flue gases of the three fuels tested. Emission factor values for each of the 9 compounds shown do not reflect the samples for which these compounds were not detected.
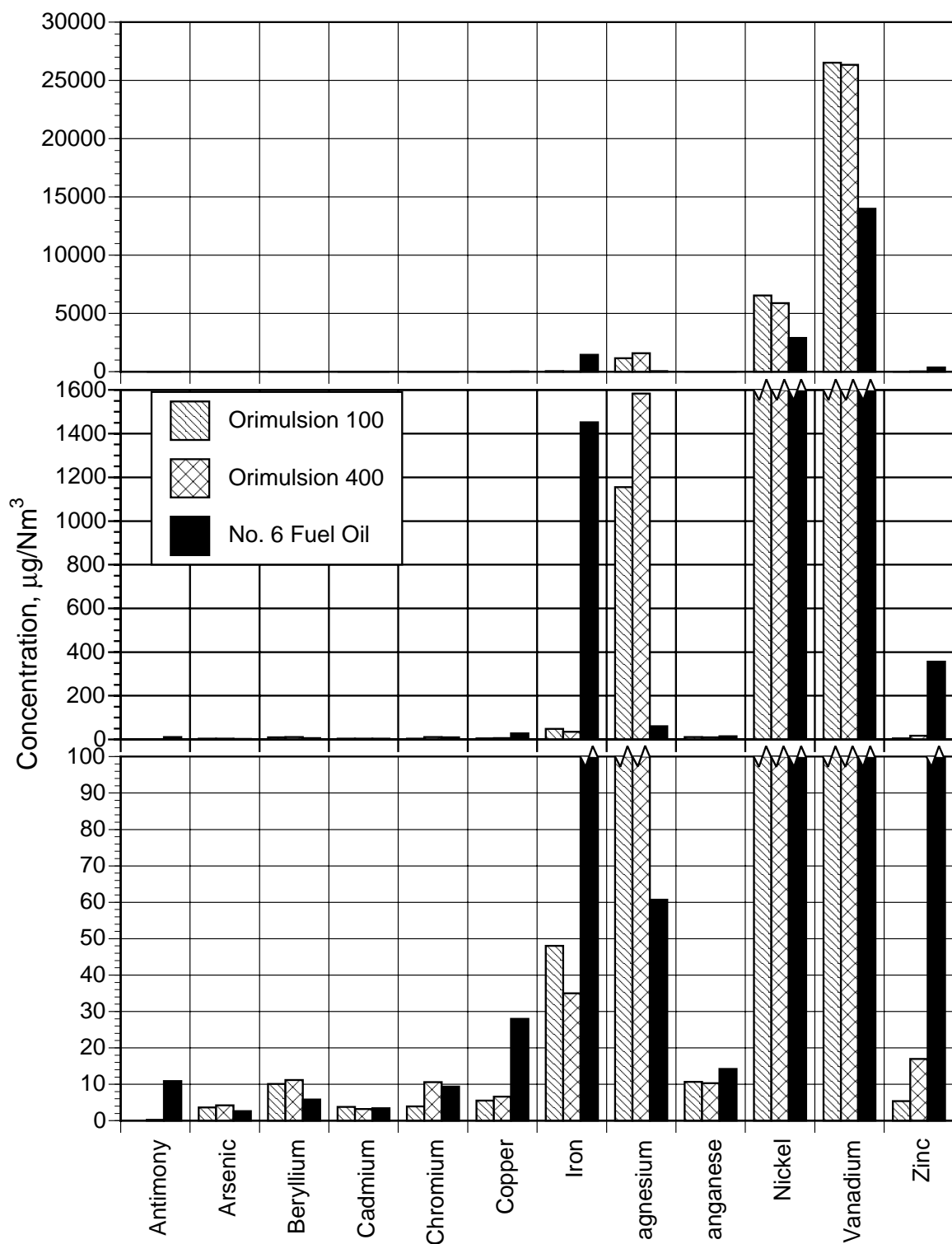
Figure 5-13. Concentrations of metals measured in the flue gases from the three fuels. The concentrations are shown on three different scales (from bottom to top): 0-100, 0-1600, and 0-30,000 µg/Nm³.

5-17

Even with the high range of recovery rates, the summary picture of trace element behavior for Orimulsion is that it behaves very similarly to the No. 6 fuel oil. Both Orimulsion formulations demonstrated higher concentrations of Mg, Ni, and V than the fuel oil, as one would expect. The fuel oil demonstrated higher concentrations of Cu, Fe, and Zn, again as would be expected. The metals for which recoveries were either very high or very low (As, Be, Cd) demonstrated roughly the same behavior in terms of recovery rates for all three fuels. Based on the current data, there is no indication that trace elements behave significantly differently in an Orimulsion-fired system than in the same system firing No. 6 fuel oil.

X-ray fluorescence (XRF) analyses of filter samples were also conducted as a further measure of the behavior of metals. These analyses were conducted by APPCD staff, and examined portions of filters from the dilution sampler (discussed in Chapter 4). XRF analyses were made of blank filters and filters with PM from each of the three fuels. In addition, filters that had originally been loaded with PM from each of the three fuels were washed with deionized distilled water (ddH$_2$O), and with ddH$_2$O and 1 M hydrochloric acid (HCl) were also analyzed. One of the key questions associated with the toxicity study was, "How soluble are the metals, particularly the transition metals Cu, Fe, Ni, V, and Zn, in the PM?"

Table 5-9 presents the results from the XRF analyses for a blank filter and filters loaded with PM from each of the three fuels. Values in the table are kilocounts per second, and represent relative amounts of each metal (higher counts are measured for higher metal concentrations). The results presented in Table 5-7 indicate that the PM captured on the dilution sampler filters (after passing through a cyclone designed to remove particles larger than 2.5 μm in diameter) contained relatively little Cu or Zn, since the XRF analyses were roughly the same for the blank filter and the filter-bound PM samples for these two metals. There were significant levels of S and lesser amounts of Fe, Mg, Ni, and V present in the PM samples, as would be expected. The Orimulsion 400 tended to have higher amounts of each of these (with the exception of Mg) than did the Orimulsion 100, and only Fe was higher for the No. 6 fuel oil compared to Orimulsion 400. These results are similar to those presented earlier from the Method 29 samples, with Fe being higher for the No. 6 fuel oil and Ni and V being higher for Orimulsion 400.

Table 5-10 presents the results for samples washed with ddH$_2$O alone or a sequence of ddH$_2$O and HCl. These results show that S is removed quite readily from the filters using ddH$_2$O alone for all three fuels. Minor differences in solubility of Fe, Mg, and Ni between the three fuels are indicated, with ddH$_2$O removing both Fe and Mg to a relatively constant level for each of the fuels. Further washing with HCl did not appear to remove any further Fe or Mg. These results indicate that Ni is removed from the No. 6 fuel oil PM sample somewhat more readily with ddH$_2$O than from either Orimulsion formulation, and that the 1 M HCl solution is required to remove Ni from the Orimulsion ash to the level attained by ddH$_2$O washing of the No. 6 fuel oil filter. The greatest difference in behavior is seen for V. About 80% of the V in the untreated filters containing PM from No. 6 fuel oil and Orimulsion 100 are removed using only ddH$_2$O, while removing only 46% of the V in the case of Orimulsion 400. Further treatment with 1 M HCl removed essentially all of the remaining V for all three fuels. This difference indicates that the PM from Orimulsion 400 may contain V in a different form than in the PM from the other two fuels, which may impact the solubility and therefore the toxicity of Orimulsion 400 PM. In general, one would expect that higher solubility would result in higher toxicity.

Emission Factors
Emission factors for CO, NO, SO$_2$, and PM in terms of mass per energy input are calculated from the concentrations of the respective compounds, flue gas flow, and fuel flow measured during testing on the PBS. Table 5-11 presents the emission factors for each of these pollutants, for the three fuels tested, in lb/10[6] Btu. These values reflect the difference both in emission concentrations as well as fuel heat content. Some differences are noticeable when emission factors are compared to emission concentrations. CO emission factors follow the same trend as did concentrations, with relatively

Table 5-8. Measured and calculated emission factors and percent recovery for 12 metals measured in the flue gases of the three fuels.

	Measured Emission Factor, lb/10^{12} Btu	Calculated Emission Factor, lb/10^{12} Btu	Recovered
Orimulsion 100 Average			
Arsenic	2.53	208	1.21%
Antimony	0	41	0.00%
Beryllium	7.06	< 0.36[1]	1960.%
Cadmium	2.67	< 0.36[1]	741.%
Copper	3.83	< 0.36[1]	1070.%
Chromium	2.76	17	16.3%
Iron	33.71	862	3.91%
Manganese	7.55	17	45.7%
Magnesium	812	24,571	3.30%
Nickel	4,600	4,957	92.8%
Vanadium	18,612	23,278	80.0%
Zinc	3.77	65	5.84%
Orimulsion 400 Average			
Arsenic	3.19	175	1.83%
Antimony	0.19	27.79	0.68%
Beryllium	8.45	< 0.40[1]	2130.%
Cadmium	2.46	< 0.40[1]	621.%
Copper	4.99	< 0.40[1]	1260.%
Chromium	7.92	15.88	49.9%
Iron	26.48	1,747	1.52%
Manganese	7.77	18.26	42.6%
Magnesium	1,185	79.39[2]	1490.%
Nickel	4,452	4,684	95.1%
Vanadium	19,932	20,800	95.8%
Zinc	12.70	29.37	43.3%

(continued)

Table 5-8 (Continued). Measured and calculated emission factors and percent recovery for 12 metals measured in the flue gases of the three fuels.

	Measured Emission Factor, lb/10^{12} Btu	Calculated Emission Factor, lb/10^{12} Btu	Recovered
No. 6 Fuel Oil Average			
Arsenic	2.35	143	1.64%
Antimony	9.65	43	22.4%
Beryllium	5.21	< 0.28[1]	1890.%
Cadmium	3.06	< 0.28[1]	1110.%
Copper	24.82	42	59.2%
Chromium	8.34	32	26.1%
Iron	1,290	2,814	45.8%
Manganese	12.59	NA[3]	NA
Magnesium	53.98	419	12.9%
Nickel	2,575	2,594	99.3%
Vanadium	12,446	12,196	102.%
Zinc	316	491	64.3%

1. The given emission factor is calculated based on the detection level of the fuel analysis method.
2. The injection of Mg additive is not included in the calculated emission factor.
3. Not available.

Table 5-9. Results of XRF analyses of untreated filters and samples, in kilocounts/second for selected metals.

Filter	S	Cu	Fe	Mg	Ni	V	Zn
Blank	0.5	0.1	2.6	0.3	0.1	0.0	27.7
No. 6 Fuel Oil	34.0	0.2	4.7	0.5	4.4	12.2	27.5
Orimulsion 100	18.6	0.2	2.7	2.5	3.0	7.6	27.1
Orimulsion 400	59.9	0.2	3.2	1.3	13.3	31.8	24.4

small differences between the two fuels, and with Orimulsion 400 slightly higher than either Orimulsion 100 or No. 6 fuel oil. For NO, the differences again are small, but the emission factor for No. 6 fuel oil is somewhat higher than for either Orimulsion formulation. Likewise, SO_2 emission factors show a slightly different pattern, with the No. 6 fuel oil having the highest emission factor, in contrast to emission concentrations where the No. 6 fuel oil had the lowest SO_2 concentration. The PM emission factor also is highest for the No. 6 fuel oil, whereas Orimulsion 400 had the highest PM mass concentration. In each case, the difference is relatively minor, and the variability in measurements makes it impossible to conclude that these differences are significant.

Table 5-10. XRF analyses of untreated and treated filters loaded with PM samples from the three fuels. Values are in kilocounts/second.

Filter	S	Fe	Mg	Ni	V
No. 6 Fuel Oil (untreated)	34.0	4.7	0.5	4.4	12.2
No. 6 Fuel Oil (ddH$_2$O)[1]	1.3	3.9	0.6	0.3	2.3
No. 6 Fuel Oil (HCl)[2]	0.7	3.0	0.6	0.3	0.1
Orimulsion 100 (untreated)	18.6	2.7	2.5	3.0	7.6
Orimulsion 100 (ddH$_2$O)	0.8	2.8	0.7	1.5	1.7
Orimulsion 100 (HCl)	0.8	2.8	0.6	0.2	0.0
Orimulsion 400 (untreated)	59.9	3.2	1.3	13.3	31.8
Orimulsion 400 (ddH$_2$O)	2.2	2.8	0.6	3.0	17.2
Orimulsion 400 (HCl)	1.1	3.0	0.6	0.6	0.2

1. Deionized distilled water.
2. 1 M hydrochloric acid.

Table 5-11. Emission factors for CO, NO, SO$_2$, and PM from the three fuels tested in the PBS, in lb/10^6 Btu.

	CO	NO	SO$_2$	PM
Orimulsion 100	0.0079	0.46	0.85	0.69
Orimulsion 400	0.0104	0.47	0.93	0.75
No. 6 Fuel Oil	0.0081	0.54	1.02	0.82

Scanning Electron Micrographs

In addition to measurements of pollutants, samples were also collected on silver membrane filters for evaluation under a scanning electron microscope (SEM) to provide morphological information of individual particles. Particles were extracted from the stack location using the same sampling system and dilution as used by the SMPS described above. However, these particles were directed through a stainless steel filter holder containing a 47 mm silver membrane filter. Sampling times of approximately 30-60 s provided a sufficient quantity of particles for analysis. Silver filters were used to improve conductivity and minimize particle charging caused by the electron beam.

The micrographs taken of samples at 700x magnification are shown in Figures 5-14 through 5-17. Figure 5-14 is an SEM micrograph of a blank filter, and clearly shows the filter fibers with little material on the filter. The fibers are 1 μm in diameter or smaller, and have no consistent orientation. Figure 5-15 is an SEM micrograph of a filter loaded with PM from the combustion of the No. 6 fuel oil, again at 700x magnification. Very few filter fibers are visible, and the filter appears to be almost completely coated with PM. The material appears to be largely composed of small hollow spheres, many with numerous pores. There also appears to be a substantial amount of ash particles similar to flakes, again with the material appearing to be quite porous. In this sample, the majority of particles appear to be smaller than 5 μm in diameter, although there are several spheres that are slightly larger, such as those at the top center and bottom center of the image.

Figure 5-16 is an SEM micrograph of a filter loaded with PM from the combustion of Orimulsion 100 at 700x magnification. The filter is again nearly completely covered with PM, although there seem to be slightly more fibers visible than was the case for the No. 6 fuel oil. The material appears to be somewhat less porous than the No. 6 fuel oil, but does have several spherical particles near the 5 μm diameter size. The spheres show some porosity, but generally less than that for the No. 6 fuel oil PM. For both the Orimulsion 100 and the No. 6 fuel oil, the PM appears to form a crust over the filter fibers, but it is impossible to say whether this crust is merely an appearance or is actually present.

Figure 5-17 is an SEM micrograph of a filter loaded with PM from the combustion of Orimulsion 400 at 700x magnification. This image appears significantly different than for either the No. 6 fuel oil or Orimulsion 100. There do not appear to be significant amounts of individual particles in this image, but more of a continuous crust or slag-type of material. There are still numerous pores in the solid, but the material appears to have solidified from a liquid rather than being deposited as many individual solid particles that later agglomerated into a crust, as was the case for the No. 6 fuel oil and the Orimulsion 100. It is not clear what differences account for the change in appearance, but the Orimulsion 400 did use a different form of Mg than did the Orimulsion 100. Whether this led to formation of different species in the particles is not known.
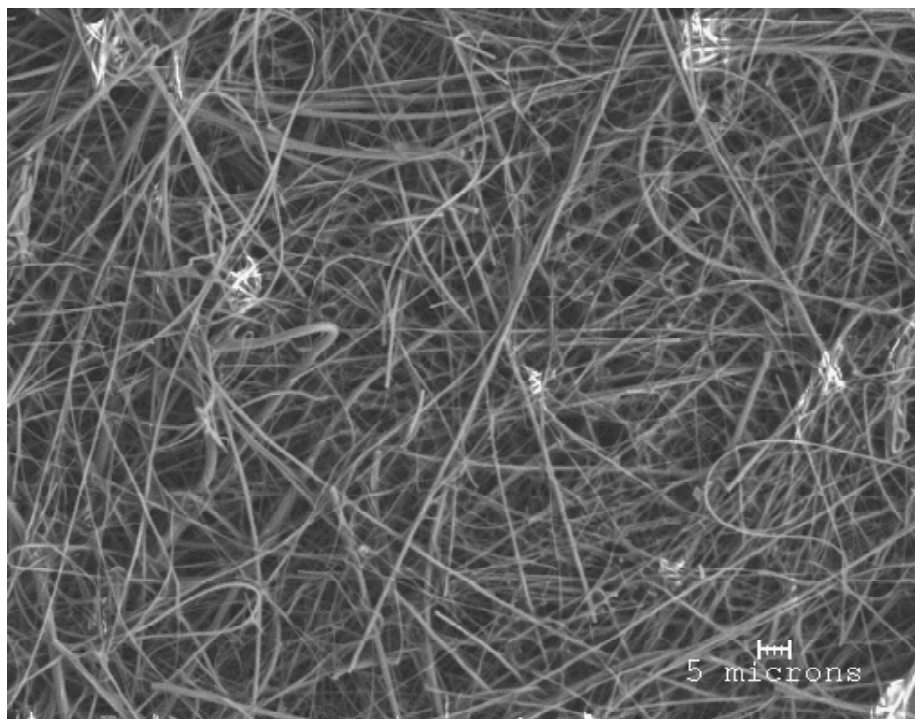
Figure 5-14. Scanning electron micrograph of untreated blank filter at 700 x magnification.
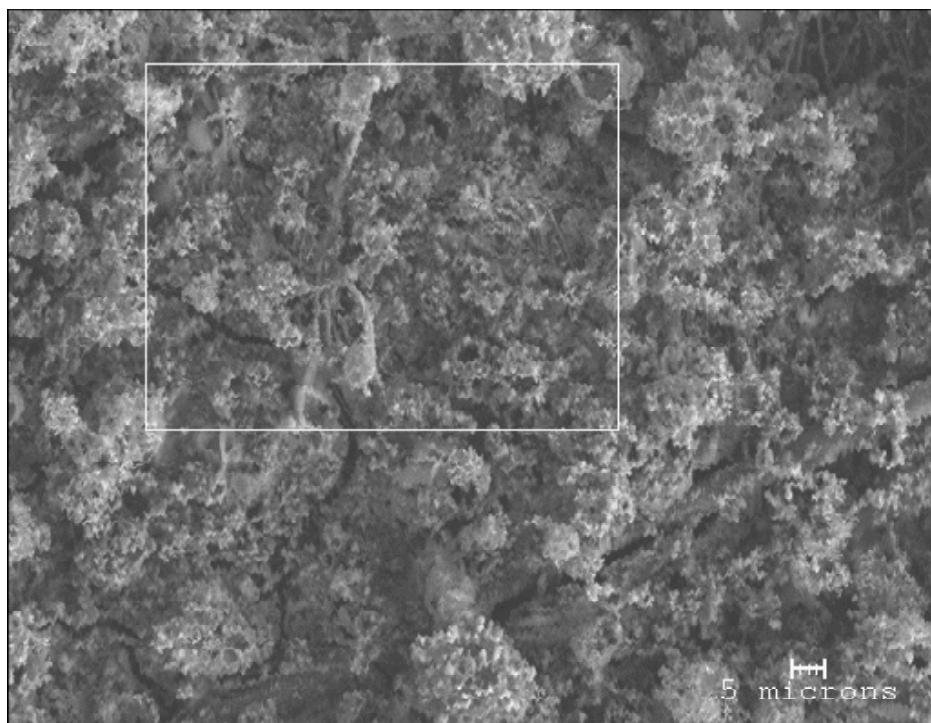
Figure 5-15. Scanning electron micrograph of untreated filter loaded with PM from No. 6 fuel oil at 700 x magnification.
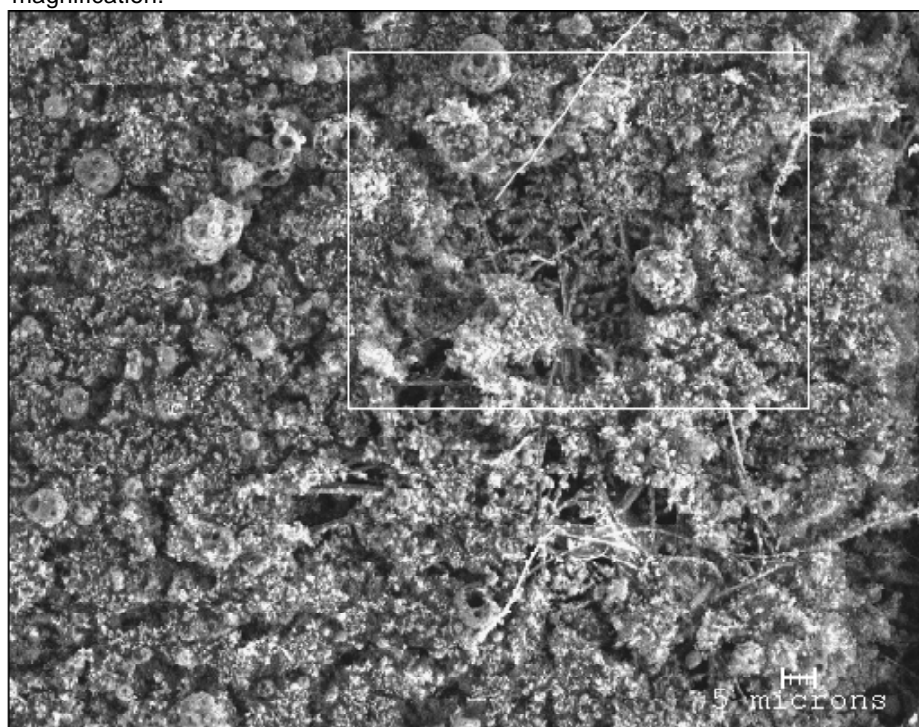
Figure 5-16. Scanning electron micrograph of untreated filter loaded with PM from Orimulsion 100 at 700 x magnification.
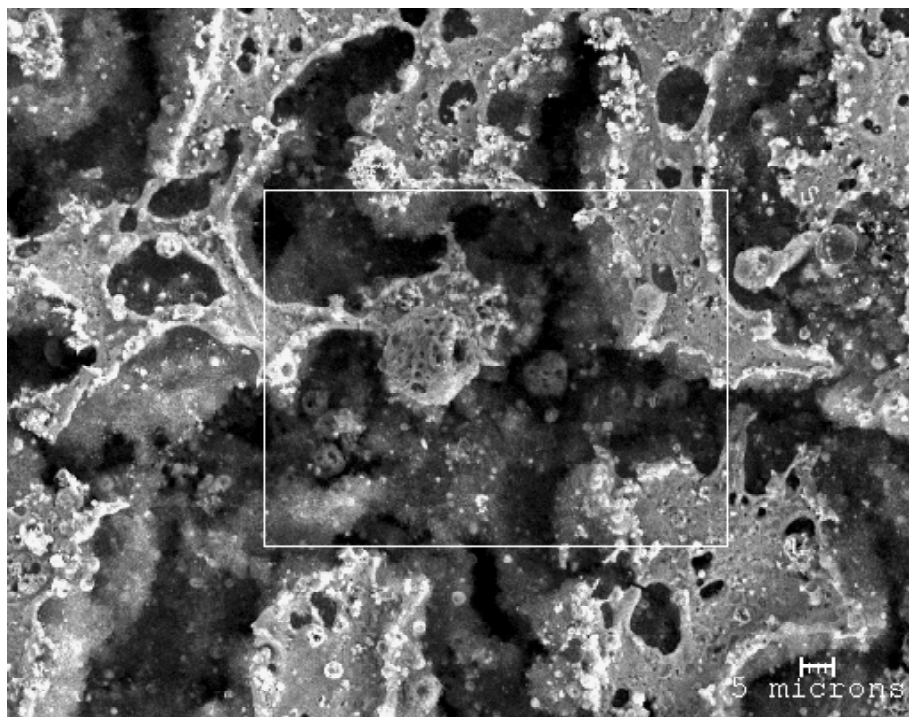
Figure 5-17. Scanning electron micrograph of untreated filter loaded with PM from Orimulsion 400 at 700 x magnification.

Chapter 6
Physicochemical Properties and Acute Pulmonary Toxicity of Orimulsion Fly Ash

Objective
Orimulsion represents a fuel made of natural bitumen emulsified in water that could be an economical substitute for fuel oils currently used in utility and other types of commercial boilers. No utilities in the United States are currently using Orimulsion, therefore, the potential public health impact associated with emissions derived from the combustion of Orimulsion has not been documented. The present study compares the physicochemical properties and acute pulmonary toxicities of fly ash obtained from the combustion of two Orimulsion formulations (Orimulsion 100 and 400) with similar properties of fly ash obtained from the combustion of a conventional fuel, No. 6 residual oil.

Oil Fly Ash Production and Collection
The production and collection of Orimulsion 100, Orimulsion 400 and No. 6 residual oil fly ash particles was performed by W.P. Linak and C.A. Miller at the National Risk Management Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC, as described in Chapter 4. Briefly, Orimulsion 100, Orimulsion 400 and No. 6 residual oil fuels were burned using a package boiler simulator as previously described (Chapter 4, pages 4-1 to 4-6). Fine ($PM_{2.5}$ mass mean aerodynamic diameter) oil fly ash particles were obtained using a dilution sampler and $PM_{2.5}$ SASS cyclone collection system as previously described (Chapter 4, pages 4-6 to 4-7). Oil fly ash particles were collected on Teflon-coated glass fiber filters. Filter samples containing Orimulsion 100 (OFA100), Orimulsion 400 (OFA400) and No. 6 residual oil fly ash (ROFA#6) were obtained for subsequent physicochemical and toxicological analyses performed by K. Dreher, Experimental Toxicology Division, National Health and Environmental Effects Research Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC.

Reference Particle
Arizona road dust (ARD) was included as a surrogate particle representing particles that may be present in the ambient air arising from mechanical processes. ARD was obtained from Andrew Ghio, Human Studies Division, National Health and Environmental Effects Research Laboratory, U.S. Environmental Protection Agency, Chapel Hill, NC. Fine ARD was produced by grinding ARD particles using a ball mill. The size of fine ARD employed in these studies was 1.491 μm mass mean aerodynamic diameter with a 1.535 geometric standard deviation.

Physicochemical Properties of Oil Fly Ash Samples and Arizona Road Dust
OFA100, OFA400, ROFA#6, and ARD samples were characterized for the following physicochemical properties: acidity; acid (1.16M HCl) soluble transition metal, lead and sulfate content; water soluble transition metal, lead and sulfate content. A summary of these physicochemical analyses is shown in Table 6-1. ROFA#6 was found to be the most acidic oil fly ash sample with the overall order of particle acidity being: ROFA#6 > OFA400 > OFA100 > ARD. Under the acid hydrolysis conditions employed, no lead (Pb) or zinc (Zn) was detected in any of the oil fly ash samples examined. Vanadium (V), nickel (Ni), and iron (Fe) were the predominant transition metals present in each of the oil fly ash samples. OFA400 contained the highest 1.16 M HCl acid soluble metal and sulfate content. The overall order of particle 1.16 M HCl acid soluble metal and sulfate content was found to be: OFA400 > OFA100 > ROFA#6 > ARD. Finally, ROFA#6 was found to contain the highest percentage of total water soluble or bioavailable metal content. OFA100 and OFA400 contained very similar and low percentages of total water soluble or bioavailable metals.

Under the combustion conditions employed in these studies, both Orimulsion formulations produced particles of higher total metal and sulfate content when compared to similar particulate emissions derived from No. 6 fuel oil. However, the water solubility or bioavailability of the various

Table 6-1. Physicochemical characterization of collected PM$_{2.5}$ oil fly ash samples and Arizona road dust particles

Sample[1]	Metal Content (μg/mg of sample)[2]							Total metal (μg/mg)	Total sulfate (μg/mg)	pH[3]
	Zn	Pb	Ni	Mn	Fe	V	Cu			
OFA100	BDL[4]	BDL	11.43 (15)[5]	0.03 (21)	0.96 (2.0)	53.84 (45)	0.01 (9.0)	66.27 (39)[6]	87.8 (100)	*4.45*
OFA400	BDL	BDL	16.79 (75)	0.03 (100)	0.94 (19)	83.91 (15)	0.01 (100)	101.68 (35)	169 (100)	*3.25*
ROFA#6	0.72 (100)	0.01 (0)	3.40 (100)	0.03 (100)	1.76 (4.6)	18.38 (64)	0.04 (100)	24.34 (68)	47.8 (100)	*2.9*
ARD	0.03 (2.8)	ND[7]	0.19 (0.12)	ND	7.01 (0.03)	0.01 (3.7)	0.08 (0.26)	7.32 (0.04)	0.26 (50)	4.97

1. Sample designations: OFA100, Orimulsion 100 fly ash; OFA400, Orimulsion 400 fly ash; ROFA#6, No. 6 residual oil fly ash; ARD, Arizona road dust, a surrogate for a non-combustion-derived particle.
2. Metal content obtained from 1.16 M HCl hydrolysis of filter samples. All values are expressed as μg/mg PM based on estimated theoretical mass deposition on filters. All metal values were corrected for filter contribution of metals.
3. pH of an aqueous solution containing equivalent concentration of 7.0 mg/mL for each sample. For comparative purposes: acidity of deionized-distilled H$_2$O, pH = 4.98; acidity of an equivalent amount of Teflon filter, pH = 5.53.
4. Below detectable limits.
5. Values in parentheses represent the percent of each metal that was water soluble. The water solubility of each metal is a measure of its bioavailability.
6. The total percent water soluble metal content for each oil fly ash sample was derived from the individual experimental data obtained for each metal.
7. Not determined.

metals were found to be lower for both Orimulsion formulations when compared to fine ROFA#6 particles. ARD particles, employed as a surrogate for non-combustion-derived particles, were not acidic and contained very little metal. In addition, the metal contained within ARD was essentially water-insoluble or non-bio-available.

Acute Pulmonary Toxicity of Oil Fly Ash and Arizona Road Dust Samples

Teflon glass fiber filters containing OFA400, OFA100, or ROFA#6 fine particles were extracted with deionized-distilled water. Water extracts containing both soluble and insoluble constituents of each oil fly ash sample were dried by lyophilization and the recovered material employed in subsequent toxicological analysis.

The acute pulmonary toxicities of OFA400, OFA100, and ROFA#6 water extracted material were examined using healthy, male, 65-75 day old, Sprague-Dawley rats. ARD was included in these toxicology studies to serve as a surrogate particle to evaluate the acute pulmonary toxicity of particles derived from non-combustion processes. Rats were exposed by intratracheal-instillation to various doses of OFA400, OFA100, or ROFA#6 water-extracted material or ARD which had been re-suspended in saline. Another group of rats were exposed to saline to serve as a control for potential trauma arising from the intratracheal-instillation procedure. Animals were analyzed for acute pulmonary toxicity by bronchoalveolar lavage at 24 hours post-exposure. Bronchoalveolar fluid (BALF) samples were analyzed for biomarkers of acute pulmonary toxicity or lung injury as listed in Table 6-2.

Results of the acute pulmonary toxicity assessments of each oil fly ash water extract and ARD are shown in Figure 6-1 and Table 6-3. A lowest observed effect level (LOEL) was determined for each sample and biomarker of acute toxicity examined in these studies. The LOEL in these studies was

defined as the lowest statistically significant dose that elicited an effect above the corresponding control saline level for each biomarker of pulmonary toxicity or injury (Table 6-2). Statistical analysis was conducted at each LOEL for each oil fly ash sample in order to produce a general relative toxicity ranking.

Intratracheal-instillation of saline was found to produce little if any detectable acute pulmonary toxicity or injury. As shown in Figure 6-1, BALF macrophage/mL levels, a biomarker of pulmonary inflammation, was not affected by any of the samples examined in this study. ARD was found to be the least toxic particle for a number of biomarkers of acute pulmonary toxicity or injury (BALF protein, albumin, eosinophil/mL) examined in these studies. ROFA#6 water-extracted material induced more pulmonary edema than extracts of OFA100 and OFA400. OFA100 and OFA400 water extracts were found to produce a similar extent of acute pulmonary toxicity or injury.

In general, under the combustion conditions employed in these studies both ROFA#6 and Orimulsion

Table 6-2. Biomarkers of pulmonary acute toxicity or injury.

BALF Endpoint	Biomarker
Protein concentration	Pulmonary Edema and/or Airway Hypersecretion
Albumin concentration	Pulmonary Edema
Lactate dehydrogenase (LDH) activity	Pulmonary Cellular Cytotoxicity
Macrophage concentration	Pulmonary Inflammation
Neutrophil concentration	Pulmonary Inflammation
Eosinophil concentration	Pulmonary Inflammation

Table 6-3. Relative toxicity of oil fly ash and dust exposures at the Lowest Observed Effect Level (LOEL) for each endpoint. Note that the rankings are not of LOEL values, but of relative toxicity (higher LOEL indicates lower toxicity).

LOEL[1] (mg/rat)	Endpoint	Relative Toxicity Ranking at the Observed LOEL[2]
**Pulmonary Injury**		
0.5	Pulmonary Edema/Secretory Activity BALF endpoint: Protein (µg/mL)	ROFA#6 > OFA100 = OFA400 > ARD = Saline
0.5	Pulmonary Edema BALF endpoint: Albumin (µg/mL)	ROFA#6 > OFA100 = OFA400 > ARD = Saline
0.5	Pulmonary Cellular Cytotoxicity BALF endpoint: LDH (U/L)	ROFA#6 = OFA100 = OFA400 =ARD > Saline
**Pulmonary Inflammation**		
0.125	Cellular Inflammation BALF endpoint: Neutrophil/mL	ROFA#6 = OFA100 = OFA400 = ARD > Saline
0.25	Cellular Inflammation BALF endpoint: Eosinophil/mL	ROFA#6 = OFA100 = OFA400 > ARD > Saline

1). The LOEL was defined as the lowest dose of each oil fly ash sample which produced a specific biological response that was statistically significantly (p<0.05) different from saline control animals.
2). Statistical analysis was conducted at each LOEL for each oil fly ash sample in order to produce a relative toxicity ranking.
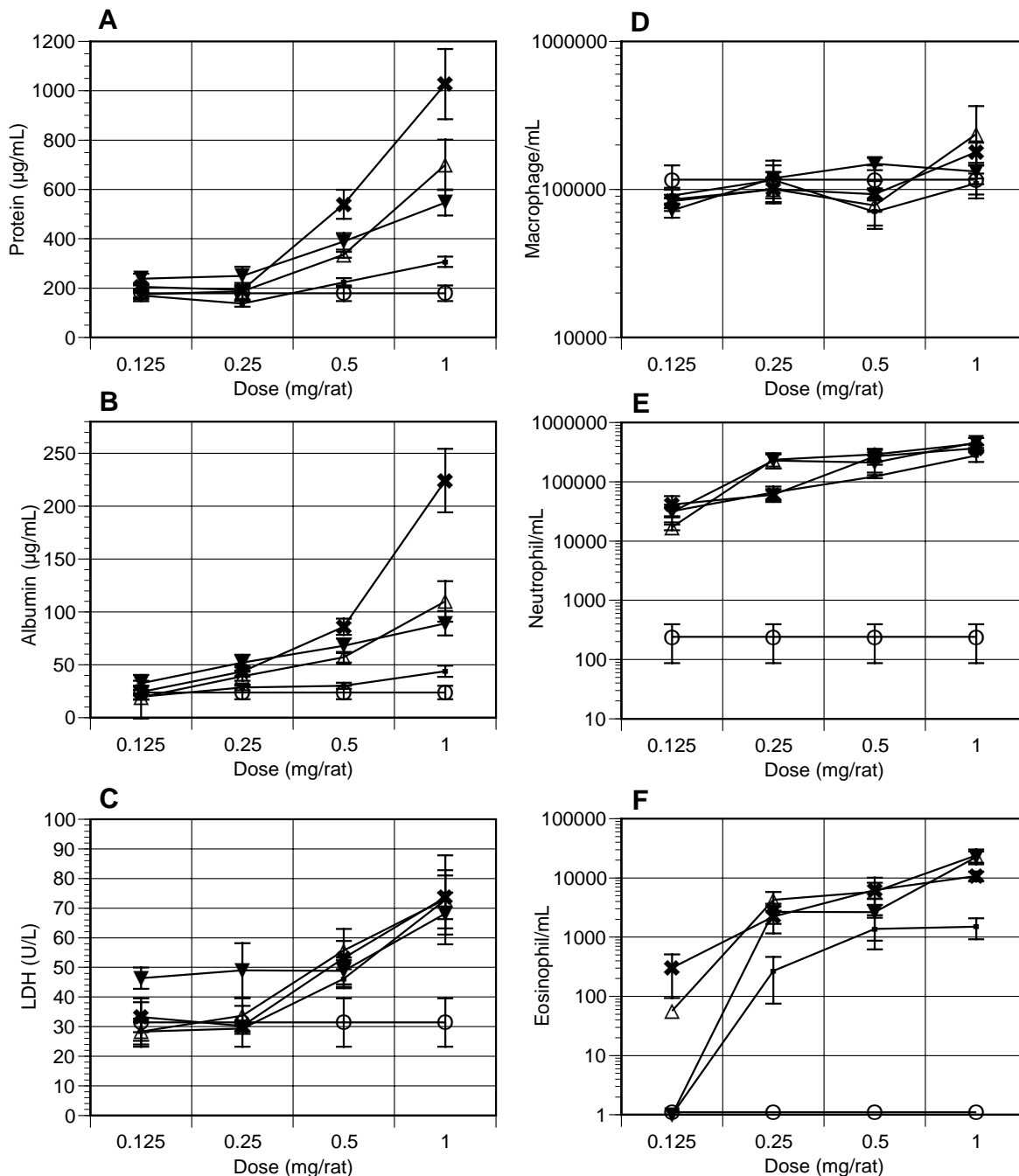
Figure 6-1. Particle-induced acute lung injury. Results obtained from analysis performed on bronchoalveolar lavage fluid samples recovered from animals at 24 h post-exposure. Animals were exposed by intratracheal instillation to: saline (O); OFA100 (△); OFA400 (▼); ROFA#6 (✖); or ARD (▪). Various biomarkers of acute lung injury were assessed such as: A) edema/secretory activity (protein/mL); B) edema (albumin/mL); C) cellular cytotoxicity (LDH U/L); as well as inflammatory biomarkers such as: D) macrophage/mL; E) neutrophil/mL; and F) eosinophil/mL. N=6 for Orimulsion 100, Orimulsion 400, No. 6 fuel oil, and Arizona road dust; N = 12 for saline. Values represent means ± standard errors of the mean.

6-4

formulations generated particulate emissions that were capable of producing significant adverse acute pulmonary toxicity. In addition, particles derived from the combustion of Orimulsion 100 and Orimulsion 400 were found to be very similar to No. 6 residual oil fly ash particles in their ability to induce acute pulmonary toxicity.

Oil Fly Ash Health Effects Commentary

There are a number of comments that need to be made regarding the health effects of Orimulsion 100 and Orimulsion 400 fly ash as reported herein. First, results obtained in these studies reflect the relative toxicities of the various oil fly ash samples, OFA100, OFA400, and ROFA#6, obtained from the combustion of these fuels using an in-house boiler located at the National Risk Management Research Laboratory, U. S. Environmental Protection Agency, Research Triangle Park, NC. It is possible that the relative toxicities of OFA100 and OFA400 versus ROFA#6 may change under different combustion conditions such as might be employed in larger utility boilers. Secondly, intratracheal-instillation was employed as the method of exposing animals to the various oil fly ash samples. This method of exposure was employed due to the small amount of material collected following the in-house combustion of the various fuels. However, comparative studies examining the relative distribution and level of acute pulmonary toxicity of oil fly ash following inhalation and intratracheal-instillation exposures have been conducted within the Experimental Toxicology Division, Pulmonary Toxicology Branch, National Health and Environmental Effects Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC. These studies have demonstrated that at low doses (110 μg/rat) similar pulmonary distribution and acute pulmonary lung toxicity following oil fly ash exposure were achieved by either inhalation or intratracheal instillation exposure methods (Costa et al. 1998). Finally, the relative toxicities of ROFA#6 OFA100, and OFA400 were determined in these studies using young and healthy animals. The relative toxicity of oil fly ash generated from the combustion of these fuels could be different when health-compromised animals are examined. Therefore, results from this study do not provide any information regarding the impact of Orimulsion 100 and Orimulsion 400 particulate emissions on potential susceptible human sub-populations.

Chapter 7
Spills

Introduction

As part of the initial activities to define the scope of this report, a workshop was held to identify the state of understanding of the environmental aspects of Orimulsion use, including its behavior and effects when spilled into water (EPA 1999a). The workshop noted that there was "an extensive body of published information on spills," although most of it was based on research sponsored by Bitor. The workshop concluded that very little information was available concerning the behavior and effects of an Orimulsion spill in fresh water, but that the primary responsibility for conducting the research necessary to supporting any application required for using Orimulsion in the U.S. rested with Bitor. The recommendations of the workshop were that if Bitor does begin to develop U.S. customers at sites accessible only by fresh water, at a site near bodies of fresh water, or at a site where fresh water can be contaminated by a spill, even indirectly, Bitor should be responsible for the research to address the data gaps as they have done for marine environments. Such research does not fall under the Congressional directive for this report, and should not be considered to be EPA's responsibility under that directive. However, since EPA is responsible for responding to spills in certain situations, the Agency should continue to investigate Orimulsion spill behavior and response as appropriate. EPA (in collaboration with the U.S. Coast Guard) has requested the National Academy of Sciences to conduct a study on Orimulsion to evaluate what additional information is required to effectively respond to freshwater spills. EPA is currently conducting smaller studies on spill behavior modeling, and will address the data gaps identified by the NAS as appropriate. For these reasons, the Orimulsion Technology Assessment Plan did not include research into the behavior and effects of Orimulsion spills into fresh water.

Background

Spills are of concern when transporting any liquid material by ship, barge, or pipeline, when leakage or accident has the potential to introduce the liquid into bodies of water near the site of material transfer or use, or when the liquid contaminates runoff or enters other indirect routes to bodies of water. Concerns about spills can be divided into two main areas: (1) spill response and cleanup; and (2) impact of the spilled material on the environment. Orimulsion has two properties that distinguish it from many other fuels from the perspective of spills. The first property that is of concern is that the bitumen portion of Orimulsion is heavier than fresh water at ambient temperatures (see Chapter 2 for discussion of Orimulsion's properties). The second property is the presence of a surfactant in the fuel, which acts to prevent the bitumen from coalescing into larger particles or spills that can be more easily collected.

The bitumen in Orimulsion has a density greater than that of fresh water (see Table 2-1). This means that Orimulsion is considered to be a "Group V oil" as defined by the U.S. Coast Guard (Federal Register 1996). Group V oils are those that have specific gravities greater than 1.0, and generally do not float on water. A committee of the National Research Council (NRC), the Committee on Marine Transportation of Heavy Oils, recently evaluated the risks of nonfloating oil spills and methods of responding to those spills (National Research Council 1999). This study included an evaluation of emulsified oils and of Orimulsion as a special case of heavy emulsified fuels.

The term *heavy oil* in the NRC report was used to describe dense, viscous oils with low volatility (flash point higher than 65 °C), very little loss by evaporation, and viscous to semisolid consistency. The report gave examples of heavy oils as including Venezuela, San Joaquin, and Bunker crude oils, residual oils (Nos. 5 and 6 fuel oil, Bunker C, and slurry oil), asphalt, coal tar, coke, carbon black, and pitch. *Nonfloating oils* is the term used by the NRC Committee to describe oils, like some heavy oils, that do not float on water. This includes oils that sink immediately, those that mix into the water column and move with the water in suspension, and those that have a portion of the fuel that initially floats, but mixes with sand or sediment and then sinks.

To date, there have been no significant spills of Orimulsion. One could estimate the probability of an

Orimulsion spill during transport based on the reported frequency of transport-related heavy oil spills; however, Bitor's policy to date has been to use double-hulled vessels for transport, which reduces spill potential. Additionally, Orimulsion has not been transported by barge, which accounts for the bulk of spill volume. The NRC study reported that the average annual movements of heavy oils were 45.7×10^9 ton-miles per year in the period 1991 through 1996. During the same time period, the annual volume of heavy oil spills was 10,840 bbl/year, resulting in a spill ratio of 237 bbl spilled per 10^9 ton-miles. Of the total, barge transport accounted for 19.6×10^9 ton-miles per year, 9,765 bbl/year spilled, and a spill ratio of 499 bbl spilled per 10^9 ton-miles (see Figure 7-1). Nonfloating oils were estimated to account for approximately 20% of the total heavy oil volume (National Research Council 1999). The spills per 10^9 ton-miles rates are likely to be higher for
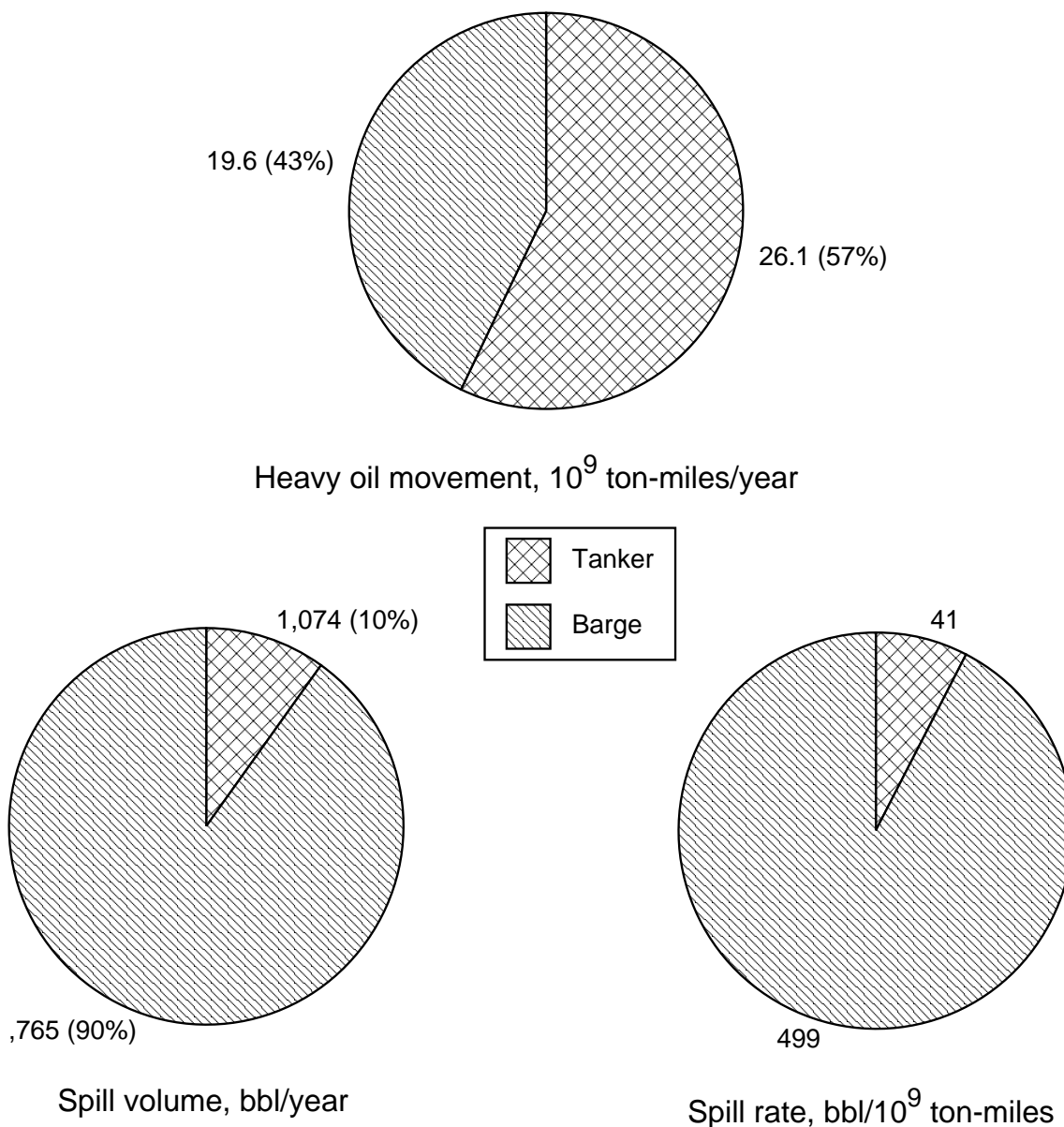
Figure 7-1. Movement, spill volumes, and spill rates of heavy oils in U.S. domestic waters between 1991 and 1996 (data from National Research Council 1999).

7-2

heavy oils than for Orimulsion due to the reliance on tankers versus barges, and the use of double-hulled versus single-hulled tankers.

It should be noted that more spills occur at stationary facilities than during transport. These spills can enter bodies of water through containment leakage, storm drains, sewers, or other indirect routes. Such spills can also pose a greater threat to public drinking water supplies, since the facilities are often located closer to populated areas and therefore nearer to water supply inlets.

The study found that nonfloating oils behave differently and have different environmental fates and effects than floating oils. In contrast to floating oils, nonfloating oils when spilled can pose "a substantial threat to water-column and benthic [sea, river, or lake bottom] resources, particularly where significant amounts of oil have accumulated on the seafloor" (National Research Council 1999). Such spills do not quickly degrade, and can impact resources for a longer period of time than do floating spills, although the effects and behavior of such spills are poorly understood. Spills of nonfloating oils are difficult to track, since the spill plume is largely underwater. While a number of tools and techniques have been developed for tracking such spills, the actual performance of these tools is unknown either through controlled experiments or application to spills. In addition, there are few technologies available for effectively containing and recovering spilled nonfloating oils. Those methods that are currently used are often effective only in areas with very low currents and minimal wave activity. Once the oil has deposited on the sea or river bed, recovery of the spilled oil can be done manually by divers (a slow and labor intensive method) or by dredging. However, dredging tends to collect substantial amounts of other sediments and materials, and proper disposal of the collected materials can be problematic (National Research Council 1999).

The surfactants present in emulsified fuels will maintain their effectiveness in fresh water longer than in salt water. Figure 7-2 shows the behavior of emulsified fuels in spills for low- and high-current fresh water and for high currents in salt water. In low-current conditions in fresh water, the spilled fuel will settle to the bottom of the water column, with low potential for mixing with bottom sediments in the short term (National Research Council 1999).

In fresh water with high currents, the bitumen particles will settle toward the bottom down-current of the spill (see Figure 7-3). The surfactant will remain effective for a limited period of time, preventing
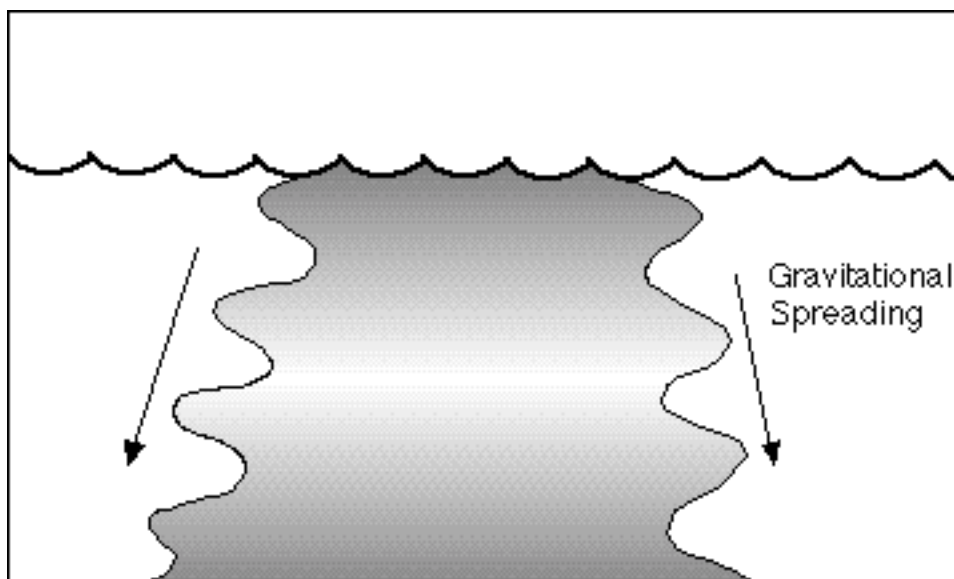
Figure 7-2. Spill of nonfloating oil in low-current fresh water (adapted from National Research Council 1999).

recoalescence of the fuel particles. The deposition rate of the particles may increase if the bitumen particles (which are highly adhesive) interact with fine-grain sediments, increasing the particles' density. In addition, many freshwater riverine systems are high in suspended solids to which the bitumen is likely to adhere. Usually, the suspended materials occur close to the bottom as a "floc." This floc once mixed with bitumen will be changed in physical/chemical character. These materials are deposited in the more quiescent submerged regions of a river.

In saltwater spills, emulsified oils will form clouds of dispersed particles in the upper 1-2 meters of the water column, as shown in Figure 7-4. In such instances, the surfactants lose their effectiveness more quickly than in fresh water, allowing the bitumen particles to coalesce and rise to the surface, forming tarry slicks. In open water, the particles are likely to disperse, resulting in increased difficulty in containing and recovering emulsified fuels as the time from the spill increases (National Research Council 1999).

Bitumen particles pose a threat in more ways than just "smothering." Many freshwater benthic inhabitants are at risk by being exposed to the fine particles of bitumen during feeding and tube building activities. Some benthic invertebrates produce membranous nets that capture the fine detrital materials that are passing by in the current. Bitumen, even dispersed bitumen, is likely to be entrapped and consumed by this type of feeding.

Reported Orimulsion Spill Studies

The NRC report cited four studies on Orimulsion spill behavior which were used to form the basis of the NRC report. These studies were largely funded by Bitor or other interested parties. The U.S. Coast Guard recently published a report (conducted by Battelle and funded by the U.S. Coast Guard Research and Development Center, and Bitor) on the behavior of Orimulsion spills (Battelle 1999). This report cites a number of studies that have been done on characterizing Orimulsion behavior in spill situations. There have also been two recent documents prepared by Environment Canada regarding Orimulsion spills in marine environments. One is a spill field guide, and the other discusses options for disposing of bitumen recovered from a spill (Owens and Sergy 1999, Guénette and Sergy 1999). The reports cited by the NRC, the U.S. Coast Guard, and Environment Canada that are specific to Orimulsion behavior are listed in Appendix F.
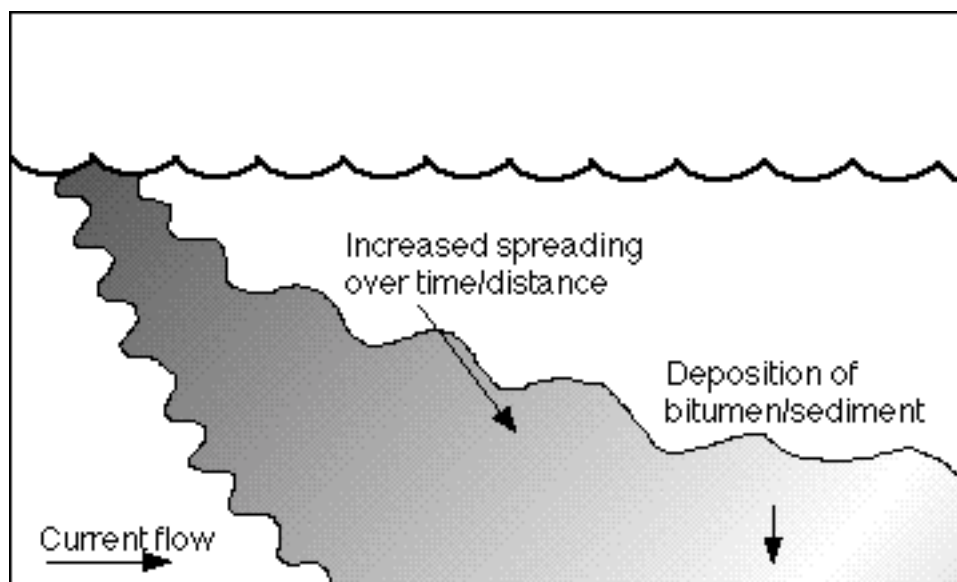
Figure 7-3. Spill of nonfloating oil in high-current fresh water (adapted from National Research Council 1999).
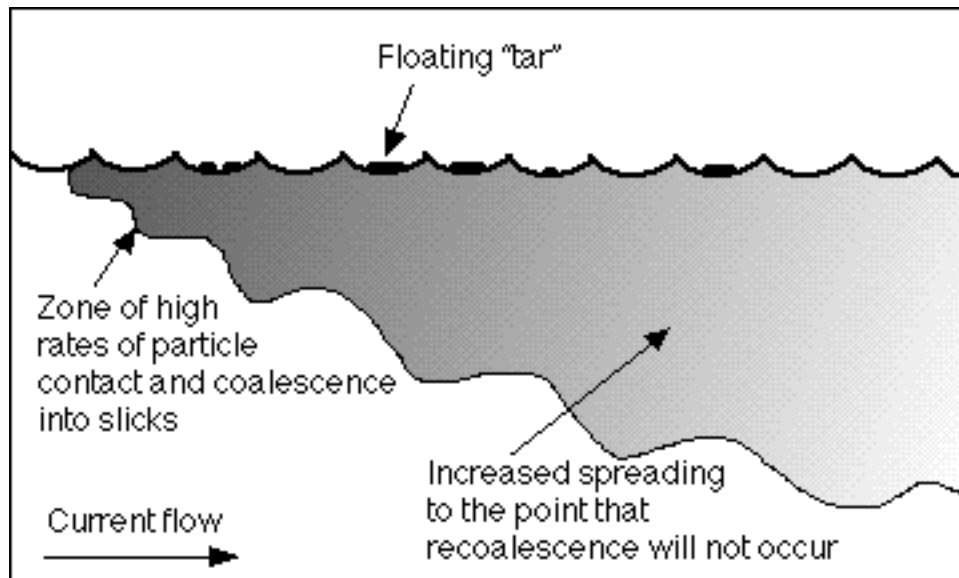
Figure 7-4. Spill of nonfloating oil in high-current salt water (adapted from National Research Council 1999).

Saltwater Spills

A number of studies of Orimulsion spills have been conducted, including containment and recovery and fate and effects studies. Most, if not all, of these studies have been funded by Bitor, and have been conducted by a range of organizations, including the University of Massachusetts, the University of Miami, Environment Canada, and the U.S. Coast Guard. To date, nearly all of this work has focused on marine (saltwater) spills. Research in the area of Orimulsion spills has largely been guided over the past several years by the International Orimulsion Working Group (IOWG). The IOWG includes members from Bitor, the U.S. Coast Guard, the Canadian Coast Guard, and Environment Canada.* These studies include investigations of spill behavior, identification of spill plume tracking technologies, evaluation of spill containment and recovery equipment and techniques, and toxicological studies of the impact to marine life of exposure to Orimulsion.

Bitor has developed methods for spill containment and recovery (Bitor America 1999), and has conducted limited open water testing of these techniques. No "real-world" test of the methods has been conducted, as there have been no spills of Orimulsion reported to date.

Special spill containment equipment designed to handle Orimulsion is on site at terminals in Canada and Denmark (Irvine and Eagles 1998, Miller and Shores 1999), as well as at other sites where Orimulsion is off-loaded.

Freshwater Spills

There is little technical information available on what happens when Orimulsion is spilled into fresh water. As noted above, Orimulsion is a heavy oil, meaning that it has high specific gravity and is likely to sink once spilled into fresh water.

Contamination of fresh water can occur during activities other than transport. Storage and handling activities at sites near bodies of fresh water such as lakes, ponds, or rivers have the potential to release

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*In the U.S., the responsibility for responding to oil spills in marine environments generally rests with the U.S. Coast Guard, with spills occurring in freshwater environments generally being the responsibility of the U.S. EPA. EPA has not participated in the IOWG.

a fuel into those bodies. Even in instances where a spill occurs at a site not located immediately next to a body of fresh water, storm drains or other means can result in indirect contamination.

Laboratory tests in fresh water conducted by Environment Canada and Battelle indicate that the bitumen particles in Orimulsion accumulate on the bottom of the test vessels with very little material remaining on the surface.

The ramifications of this behavior are many:

(a) If Orimulsion behaves in a freshwater body as it does in the laboratory, then the bitumen particles can sink through the water column and be deposited on the bottom, downstream from the spill location. Orimulsion is not a liquid but a heavier-than-water suspension which dissipates once spilled. The impact from this behavior would likely be the smothering of benthic organisms living on or in the sediments. The Battelle study indicated that the bitumen fraction of Orimulsion would sink to the bottom under calm water situations, and that in low energy situations, dilute Orimulsion remained in suspension. The new data suggest that pelagic (open-sea) species may also be vulnerable if low energy levels keep Orimulsion in suspension (Battelle 1999).

(b) Oil spill cleanup technology is based upon removing the spilled product from the water surface and contaminated surfaces. Subsurface removal of a sunken product is limited to accumulations in distinct pockets, indentations, or depressions. The lighter-than-water spilled product sometimes is entrained and adheres to bottom substrates, e.g., cobble, algae and aquatic vegetation. This product will often float to the surface if disrupted and dislodged where conventional equipment can remove the product from the surface. Orimulsion does not have the same physical properties and will not resurface in fresh water.

Castle et al. (1995) characterized fate and transport mechanisms and removal techniques for sunken oils. The assessment procedures mentioned in their paper are more applicable for marine waters but have some application for the freshwater environment. They stressed the importance of field observations made from aircraft and predictive models to ascertain the probable fate and transport of a spill of heavier-than-water petroleum product. Accessing expertise in local resource and navigation offices can be helpful in determining sinks and collection spots on the bottom of a receiving water body. An assortment of geophysical instruments and techniques have been shown to be valuable in locating and mapping submerged product.

Physical removal of bitumen is currently limited to a subsurface operation using divers and vacuum hoses. Limited success for containing bitumen using fish netting was observed in tests performed in a wave tank in Canada (Brown and Goodman 1989). In these tests, bitumen leaked through the netting being towed at 0.3 m/s (0.77 miles/hour), indicating that in currents carrying spilled bitumen at greater than 0.3 m/s, bitumen would not be completely trapped and contained. A spill of fresh Orimulsion would even be harder to trap and contain due to the smaller particle size of the bitumen/surfactant.

Many conventional oil booms will begin to leak under the boom (i.e., entrain) at about 0.75 knot. In higher currents, the booms can be placed at an angle to the current (i.e., deflection booming) so that the normal current to the boom is below 0.75 knot. This prevents the boom from leaking and allows the operator to divert the oil to a quieter area where it can be removed from the surface with conventional skimming equipment. These techniques may possibly be employed with an Orimulsion spill by deploying booms below the surface to collect and then recover the bitumen using vacuum pumps. However, no tests of this approach have been documented.

Several technologies for recovery of Orimulsion and Orimulsion bitumen in fresh- and saltwater environments are in various stages of development (Bitor America 1997, 1999;

Lorenzo 1996). However, one of the areas of concern for these experimental recovery systems is their "scalability." As the Orimulsion becomes more dispersed, more water must be pumped through the system with the Orimulsion. While these approaches may be reasonably effective in the lab, the question remains as to how effective they will be when pumping large quantities of water through them in an actual spill. Further, none of these techniques have been demonstrated in riverine environments, which require different approaches and in some cases different technologies compared to open water spill recovery methods.

The lack of case histories of Orimulsion spilled into fresh water leaves speculation and assumptions as to the fate and transport of this product. Considering the state of the knowledge and practices for oil spill cleanup, which is geared primarily toward removing surface oil, the degree of success for removing subsurface deposits of spilled Orimulsion remains an open question. In the absence of more information, a conservative assumption is that an Orimulsion spill will defy cleanup by conventional means and the material will therefore remain intact in the environment.

(c) Orimulsion is composed mostly of bitumen, which is a complex mixture of hydrocarbons and is similar in handling and content to liquefied asphalt (Deis et al., 1997). Some of the hydrocarbon compounds associated with this fraction are known carcinogens; e.g., benzopyrenes (Jokuty 1999). One of the dangers of a spill of Orimulsion into a major freshwater body would be the threat presented to public water supplies. Most public water supply intakes are submerged. A submerged plume of spilled Orimulsion moving downstream could intercept an intake pipe and be drawn into the supply, especially if the plant operators had not been warned beforehand to cease pumping. A slug of Orimulsion could potentially overwhelm a water supply treatment capacity for removing organics including some of the carcinogenic compounds mentioned above. Most plants are set up to remove settlable solids and low concentrations of organics but not heavier-than-water liquids or suspensions; e.g., heavy oils, Orimulsion.

Data Gaps

As the above sections show, a number of data gaps exist with respect to understanding the behavior and fate of Orimulsion spilled in fresh water. Because of the significant increase in cost associated with transfer of the fuel from ocean-going tankers to barges or other means of transport, Bitor's current plans are to develop U.S. customers only at sites accessible by ocean-going tankers. Nevertheless, understanding the behavior and fate or Orimulsion in fresh water is important due to the presence of streams, wetlands, and other bodies of fresh water near a site that receives Orimulsion by ocean, and because of the potential for Orimulsion to enter bodies of fresh water through indirect routes such as storm drains. Any freshwater bodies near a site using Orimulsion may be impacted by a spill that occurs during fuel handling or other activities not associated with marine shipment.

As noted in the Orimulsion Technology Assessment Plan (EPA 1999a), if Bitor does begin to develop U.S. customers at sites accessible only by fresh water, at a site near bodies of fresh water, or at sites where freshwater contamination may occur (even if indirectly), Bitor should fund the research to address the data gaps as they have done for marine environments. Such research does not fall under the Congressional directive for this report, and should not be considered to be EPA's responsibility under that directive. However, since EPA is responsible for responding to spills in certain situations, the Agency should continue to investigate Orimulsion spill behavior and response as appropriate.

EPA and the Coast Guard have initiated a study on Orimulsion by the National Academy of Sciences to evaluate the information needed to develop an effective Orimulsion spill response. EPA will use this guidance to determine what additional research may be required to support their regulatory requirements with regard to spill response. Other work on Orimulsion is being carried out within EPA's Office of Research and Development to more fully characterize specific chemical and physical properties of Orimulsion and to evaluate a spill behavior model and extend the model to cover Orimulsion.

Chapter 8
Environmental Risk Assessment

This chapter contains two major sections. The first was prepared by EPA's National Center for Environmental Assessment (NCEA), and is an evaluation of a previous study on risk and environmental impacts associated with marine spills of Orimulsion. The second section was prepared by EPA's National Risk Management Research Laboratory (NRMRL), and compares Orimulsion to a heavy fuel oil in the context of a health risk assessment of exposure to hazardous air pollutants generated by electric utility steam generating units.

Comparative Ecological Risk Assessment Evaluation
As part of the Orimulsion Technology Assessment Plan, an evaluation of the primary environmental studies on the risk and environmental impacts of marine spills associated with Orimulsion was identified as a topic to be included in the Assessment Plan. NRMRL requested that the EPA National Center for Environmental Assessment (NCEA) lead this task. NCEA scientists decided that an evaluation of the major ecological risk assessment conducted on Orimulsion, by external reviewers and EPA scientists, would provide the most information on the environmental impacts of a marine spill of Orimulsion. The primary ecological risk assessment on Orimulsion 100 was led by the University of Miami to compare the risks associated with a spill of Orimulsion 100 to those of a spill of No. 6 fuel oil to the Tampa Bay, Florida, ecosystem. The results of this effort are contained in Harwell et al. (1995) and Ault et al. (1995). Further, the University of Miami team conducted additional studies to expand the ecological risk assessment in support of the licensing process followed by a Florida utility seeking to use Orimulsion in the Tampa Bay, Florida area. These additional studies are listed in Appendix G. In support of the Orimulsion Technology Assessment Program, NCEA scientists identified key assessment issues, developed a charge to the reviewers of the Harwell study, and selected three reviewers to address these issues in their evaluation of the documents.

The Harwell assessment evaluated by NCEA did not examine in detail the potential physical effects of spilled Orimulsion, which have the potential to be as serious as toxicological effects. The NCEA evaluation examined only a single study and not the larger body of literature on Orimulsion spills, and did not discuss factors outside the scope of the Harwell study that may have additional significant ecological and health impacts.

This evaluation contains three sections: an introduction of the topic and NCEA's role in the effort; a summary of the approach for the comparative ecological risk assessment conducted by Harwell et al. (1995) and their conclusions as to the comparative ecological risk between the use of Orimulsion 100 versus No. 6 fuel oil; and a scientific evaluation, by the external reviewers and EPA scientists, of the comparative ecological risk assessment. The reviewers' comments address assessment methodologies, portability of the assessment, fate and transport methods, toxicity methods, and research needs.

Introduction
Orimulsion is a new compound in the environment and it has unique aspects to consider. For example, the density of Orimulsion is important when determining the transport and fate of the material in marine, brackish and freshwater systems. Also, organisms or ecological resources most at risk from releases of Orimulsion may be different from biota at risk from oil spills. In addition, the delivery of the material in toxicity studies to assess effects of this compound on aquatic life requires special attention to ensure the exposure is similar to what could occur in marine systems.

The comparative assessment conducted by Harwell et al. (1995) was funded by Florida Power & Light. Florida Power & Light applied for a permit to burn Orimulsion 100 at their Manatee Parrish power plant located on Tampa Bay, Florida. The power plant currently burns No. 6 fuel oil, and a comparative assessment was one of several studies funded by the utility. Florida Power & Light's request for a permit to burn Orimulsion 100 at their Manatee Parrish power plant was denied for policy reasons on June 24, 1998.

Summary of Comparative Ecological Risk Assessment Reports

The comparative ecological risk assessment conducted by Harwell et al. (1995) and the related technical support document (Ault et al. 1995) on environmental impacts of spills associated with Orimulsion 100 versus No. 6 fuel oil in the Tampa Bay ecosystem were determined to be of sufficient depth and quality to appropriately describe the ecological risks to marine systems and to the Tampa Bay ecological system in particular. This determination was made by the external panel and was reviewed by NCEA. The comparative ecological risk assessment incorporated much of the pertinent environmental fate and effects studies available on Orimulsion 100. The accompanying technical support document (Ault et al. 1995) generated or reviewed much of the aquatic and terrestrial toxicity data, the environmental fate and transport data, geographical information systems (GIS) techniques, and the modeling data. The assessment utilized state-of-the-art methods, presented new approaches and scientific advancements, and applied appropriate ecological risk assessment techniques, following the ecological risk assessment framework (Rodier and Norton 1992), to compare the environmental impacts from various spill scenarios of Orimulsion 100 and No. 6 fuel oil.

Scope of Harwell Work

The project (Harwell et al. 1995) consisted of:
1. developing sophisticated modeling tools to simulate dynamically the physical environment of Tampa Bay;
2. establishing geographical information and scientific data visualization systems to collate an extensive database on the ecology of Tampa Bay and its biological resources into a spatially distributed, graphically appealing system;
3. conducting experiments to test toxicological responses of biological resources to No. 6 fuel oil and Orimulsion 100 in addition to the survey of existing toxicological data;
4. applying stochastic models of population-level toxicological effects;
5. developing scenarios of hypothetical conditions that might occur at the time of a spill of No. 6 fuel oil or Orimulsion 100;
6. applying models to develop maps of estimated concentrations and exposures of toxicologically important constituents of each fuel type;
7. analyzing the co-occurrence of exposures with distributional data of selected fish and invertebrate species of Tampa Bay;
8. analyzing the fate and shoreline impacts of the slick that would ensue from a spill of No. 6 fuel oil;
9. calculating the risk of ecological effect from the water and shoreline exposures to the two fuel types; and
10. synthesizing analyses into an overall judgment of the comparative ecological risks of No. 6 fuel oil and Orimulsion 100 spill in Tampa Bay.

Approach of Harwell Work

The approach chosen by Harwell et al. (1995):
1. was conservatively protective by choosing parameters that were plausibly conservative for the scenarios used;
2. studied species and life stages that were sensitive to the stress and important to society;
3. examined potential effects on populations and critical habitats;
4. emphasized cumulative exposures on ecotoxicological endpoints using plausibly conservative assumptions; and
5. utilized sensitivity analysis to evaluate changes in key factors on the magnitude of the ecological effects.

Conclusions of Harwell Work

The conclusions reported by the authors of the comparative ecological risk assessment of the two materials (Harwell et al. 1995) determined that the ecological risks from No. 6 fuel oil and Orimulsion 100 to the Tampa Bay ecological system are essentially similar. Their assessment demonstrated that, while the materials have the likelihood to impact individual ecological endpoints differently (e.g., spotted sea trout versus coastal systems), the overall risks were judged, by the authors, to be comparable. If No. 6 fuel oil risks are assumed to be socially acceptable, since a power plant is currently utilizing No. 6 fuel oil, then the overall ecological risks from Orimulsion 100 would not be significantly greater. There is greater uncertainty about some of the effects on aquatic systems

from Orimulsion 100 because it does not have an extensive data base. A synopsis of the comparative risk methodology is presented in Appendix H.

Orimulsion 100 and No. 6 fuel oil impact ecological endpoints differently. In the comparative risk assessment conducted by Harwell et al. (1995), the risks of the two materials to biota in the water column, coastal systems, and avian species were evaluated. Water column risks from Orimulsion 100 exceed those from No. 6 fuel oil. The lower amount of No. 6 fuel oil that enters the water column, combined with a shorter residence time, results in a lower cumulative exposure. After a spill, Orimulsion 100 will be dispersed into the seawater column and it will therefore have a longer cumulative exposure. However, fuel oil contains much higher levels of dissolved aromatics than Orimulsion 100. These dissolved aromatics cause much of the toxicity to aquatic life. Therefore when ecological effects in the water column are compared, Orimulsion 100 has only a slightly higher toxicity. The ecological impacts from the fuel oil slick on coastal systems and avian species will be significant for some spill scenarios of No. 6 fuel oil. Orimulsion 100 spills will have limited effects on these endpoints (Harwell et al. 1995).

Scientific Evaluation of the Comparative Ecological Risk Assessment of Spills from No. 6 Fuel Oil and Orimulsion 100

The comparative ecological risk assessment (Harwell et al. 1995) and the related technical support documents (Ault et al. 1995) were evaluated by EPA and external scientists for technical adequacy, technical approach, and research needs. Their comments are summarized in the following categories: assessment methodologies, portability of the assessment to other sites, fate and transport methods, toxicity test methods, and research needs.

Overview of Harwell Assessment

Overall, this comparative ecological risk assessment (ERA) was impressive in its scope, level of research effort, and use of innovative approaches for estimating and understanding risks. The approach taken by the investigators was also well-conceived and well-documented in its prediction of the environmental distribution and consequences of compounds resulting from a spill of each fuel in Tampa Bay. Use of dynamic fate and transport models, geographic information systems, extensive toxicity testing, and other tools in this assessment puts it ahead of most assessments that have been reviewed in the past. Reviewers agreed with the authors' major conclusion that a spill of Orimulsion 100 likely poses a similar or lower risk to Tampa Bay biota than does an equivalent spill volume of No. 6 fuel oil. However, parts of the assessment, such as risk characterization, population modeling, and impacts to benthic (sea-, lake-, or river-bottom) communities, were identified by reviewers as assessment topics that could be improved. These improvements would enhance the present report, however they do not impact the conclusions put forward by the authors. The research needs section identifies research and modeling studies to address these issues.

Assessment Methodologies

Questions 1, 2, and 3, in this section come from the NCEA charge to the reviewers.

Question 1. How well does the Harwell et al. (1995) document present models, techniques (GIS, sensitivity analyses, population models, etc.), and experimentation to assess the ecological risks associated with marine spills of Orimulsion 100?

The document generally describes appropriately applied models, techniques, and experimentation. Overall, they are consistent with the current state-of-the-art methods and, more importantly, generally apply appropriate technology to address the relative risk of Orimulsion 100 and No. 6 fuel oil. As a model of what can be done with ecosystem assessment and toxicological information, the state-of-the-art-modeling procedures and the combination of GIS and data visualization approaches are an exceptional management tool. The use of GIS to illustrate the outputs of the hydrodynamic and fate modeling, levels of hydrocarbons and aromatics following spills of Orimulsion 100 and No. 6 fuel oil, abundances of different fish species, etc., is an excellent means of helping readers visualize spatial patterns. However, the GIS tool could have been used more effectively and the results better presented by providing more text to support the graphics.

Although consistent with current methods, standard toxicity test results are mathematically limited information with which to imply population effects and to convert toxicity metrics to population

model parameters. The toxicity data are mathematically limited for use in the matrix-based demographic and metapopulation-based models. Approximations were attempted (e.g., applying a logistic model with assumptions of a probabilistic process for lethality or exponential death through time due to toxicant action [Ault et al. 1995; pp. 8-24 and 8-42]) that are not generally valid for many situations. It would have been preferred if the test results had been used to generate survival time information based on exposure concentration and duration of exposure.

Joint distribution analysis can also be considered a state-of-the-art tool because it can be used to estimate probabilities of effects of differing magnitudes (referred to as risk curves). Risk curves present a great deal of information to risk managers and stakeholders, much more so than risk quotients. In this assessment, however, the joint distribution approach was used to generate risk quotient distributions. The same information is required to generate probabilistic quotients and risk curves (an exposure distribution, a concentration-response relationship), yet the latter is much more informative than the former. Generation of risk curves is a research need that would improve the assessment. This research need is not limited to risk assessments for Orimulsion, but, rather, is a general need for the field of ecotoxicology.

Satisfying all the assumptions to determine risk to ecological communities is very difficult. Although it also carries some dubious assumptions, a species sensitivity distribution approach producing a HC5 and associated 95% confidence interval could have been used. Although imperfect evidence, it could have been helpful in evaluating this assessment. The present assessment used a Monte Carlo-generated "joint" distribution of hazard quotients that is reasonable and similar to the suggested approach. However, neither approach satisfies all assumptions needed to determine risk to an ecological community.

The rationale for the decision that "the exposure and effects data were treated as log-normal distributions in the analyses" (Harwell et al. 1995; p. 133) is unclear. There are good theoretical reasons for treating exposure as a log-normal distribution (see Ott 1995), but probably none for treating the effects data as such. Generally, the appropriate underlying distribution for effects data is the binomial distribution for quantal endpoints (e.g., mortality), the Poisson distribution for count endpoints (e.g., number of young), and the normal or Gaussian distribution for continuous endpoints (e.g., growth rate, biomass) (Bailer and Oris 1997).

Sensitivity analysis is a very important tool for risk assessment, particularly in probabilistic risk assessments, and it appeared to be used effectively. It would have been useful to see figures of model sensitivity results that allowed easy comprehension of the relative level of influence of the major variables on model prediction outcome. The authors made extensive use of sensitivity analysis in this assessment to investigate, for example, the influence of location, timing, season, climate (e.g., wet season, dry season), and other variables on the resulting spatial distribution of plumes from spills of Orimulsion 100 and No. 6 fuel oil. Size of spill was also briefly considered (i.e., comparison of spills of 10,000 and 25,000 barrels). Some parameters expected to be important in estimating spill risks (e.g., spill duration in the 3-D hydrodynamic model; dispersion coefficients, degradation rates and physicochemical properties in the SIMAP fate and transport model) were held constant, so their influence on outputs could not be investigated through the use of sensitivity analysis. Although the use of the stochastic RAMAS population model should have been amenable to sensitivity analysis to determine important input parameters, reviewers could not find any such analysis in any of the supporting documentation.

The linkage to population risk is central to a meaningful ecological risk assessment. The authors recognized this and spent considerable effort trying to do this. In this context, the present assessment is much better than most assessments. While population-level modeling was done to assess potential effects on population abundance for sea trout and other species, population modeling could have used the available information effectively through linkage to stock management models, better utilization of lethality data, and providing better rationales for assumptions and equations. It would have been interesting to compare estimated population losses from a spill versus recreational and commercial fishing. The production of survival functions would have been relatively straightforward from the generated data and would have utilized the mortality data more effectively. The extrapolation from lethal concentration to 50% of exposed population (LC_{50}) to dose response curves with dubious relationships to predict effects at different exposure durations on mortality, could have

been improved through the use of the generation of survival functions with time (i.e., time to event). More discussion on the use of assumptions and equations (e.g., exponential mortality with time due to toxicant effect; focus on lethal effects in demographic analyses; operationally assuming that the most sensitive stage of an individual's life is the most important to consider in population viability analysis) would have been beneficial.

Question 2. Are assessment endpoints and measures of effect appropriate for this site? Are they linked in the risk characterization section?

The document did a good job developing selection criteria for the assessment endpoints and linking them to appropriate metrics (measurement endpoints). While population-level impacts were modeled, it would have been helpful for risk communication and translation among resource managers if the document could have provided estimates of yield reduction in the context developed by fisheries stock assessors. Given the selection of sea trout as the focal species for the risk assessment, due to its status as the most sensitive species, but also with important commercial and recreational value, it would have helped to incorporate the "take" from a spill into terms of a fisheries stock management model. Placing spill "take" into the same context as takes from recreational and commercial fishing would have been helpful in assessing the relative magnitudes of these demands on the population. Information on the sea trout stock remaining well above the level of sustainable harvest after a spill scenario would be useful. However, this is not a major flaw and its omission did not detract from the generally insightful and thorough job done here.

The general focus in this assessment was on estimating risks of spills to spotted sea trout, although considerable effort was also directed at estimating risks to other biota such as sea grasses, mangroves, aquatic invertebrates, and other fish species. The general arguments presented in the problem formulation for selecting these species seem well supported. However, key pieces of the problem formulation thought process are scattered throughout Volume I of the assessment (Harwell et al. 1995). For example, the rationale for key species selection was presented at the end of the analysis section (Ault et al. 1995; pp. 98-99) and the details of what actually was selected were not provided.

The assessment endpoints and measures of effect chosen for this site seem appropriate (e.g., meet the criteria of potentially exposed, sensitive, and of ecological, social and economic value), and the assessment endpoints were appropriately considered in the risk characterization phase. The risks of spills posed to endangered species could have been more directly addressed, although clearly no toxicity tests can be done on endangered species or on marine mammals. As the authors correctly note, many populations can recover quickly from acute toxic effects because of source refugia outside the spill area. However, with endangered species, particularly those that would recover very slowly from a spill impact (e.g., manatees), acute toxic effects to individuals within the spill area could be devastating at the population level. It would be useful for the authors to identify which endangered species are at risk in and near Tampa Bay and to at least qualitatively consider the risks spills would pose to these species.

The statement is made about developing a metric assuming that "The contribution that a given species makes to the total abundance of Tampa Bay's fish and invertebrate fauna provides insight into its ecological position and function in the ecosystem. From this perspective, the relative abundance or density of a given species represents a simple index of its importance." (Ault et al. 1995; pp. 8-34). Given numerous examples to the contrary (e.g., keystone species) and the different ways that abundance is measured (e.g., number of individuals, biomass, coverage), this section could be rephrased.

Question 3. Does the risk characterization appropriately present the risk estimate and discuss the comparative risk fully? Are the conclusions of the comparative assessment supported by the risk characterization presentation?

The breadth of methods employed to characterize risks of Orimulsion 100 and No. 6 fuel oil spills was truly impressive. Given the data and analyses developed, the conclusions were supported. Reviewers supported the conclusions that Orimulsion 100 presents slightly greater water column risks than does No. 6 fuel oil, but that the risks of a fuel oil slick to shoreline and tidal communities likely exceed the water column risks posed by Orimulsion 100. However, the presentation of the risk

characterization section could have been improved. Often key details were missing and assumptions were not justified.

The analysis is very ambitious and provides a comprehensive assessment of the behavior and toxicity of the two fuel types. The conclusion from the analysis is that the ecological risks associated with spills of either No. 6 fuel oil or Orimulsion 100 are comparable. This is based on the lack of demonstrated phytotoxicity to mangroves and sea grasses; the normalized exposure fields for each fuel type; and the model predictions of physical transport. Orimulsion 100 is considered to behave like "pre-dispersed" oil and much of the interpretation of physical fate and toxicity is based on the assumptions that the exposure field (toxic concentrations and time) of the two fuel types will be comparable. This is due primarily to the relatively high toxicity but short duration of the aromatic fraction of No. 6 fuel oil and lesser toxicity but longer duration of the total hydrocarbon fraction of Orimulsion 100. The authors then conclude that the longer term effects associated with spills of No. 6 fuel oil reported in the literature would not likely occur with Orimulsion 100 due to the lack of sediment accumulation of hydrocarbons from Orimulsion 100. This latter statement was addressed in subsequent studies listed in Appendix H.

Several statements in the risk characterization section make expert judgments without enough explanation for the decision presented to the reader. For example, in the documents (Harwell et al. 1995; pp. 110 and 114) it is stated that selection of sea trout and silversides as focal species effectively bounds the range of expected effects to aquatic biota in Tampa Bay. Further information is needed to explain how the figure (Harwell et al. 1995; p. 124, Figure V7) provides evidence that "some population impacts would be experienced over a significant area." The figure merely shows what proportion of the Bay would be exposed to Orimulsion 100 or No. 6 fuel oil following hypothetical spills at four locations. How this translates to population level effects is never explained.

The comparative risk was based on identical scenarios (Harwell et al. 1995). A reviewer did not accept the "common conditions" characteristic of the comparison process. It may be a useful comparison if the selected scenario is benign for one fuel and negative for the other; yet, with another scenario, the relative impacts were reversed. Alternatively, one could pick "the most probable" scenario and use that for comparison; this would also require an estimation of the variation expected from the associated predictions. In a comparative risk assessment, relative risks, odds ratios, or risk ratios could have been applied very effectively for the No. 6 fuel oil versus Orimulsion 100. However, the report (Harwell et al. 1995) strongly argued and the administrative law judge agreed that a comparative ecological risk assessment, examining the relative risks of two different fuels, must have identical scenarios in all regards except for the fuels themselves in order for a valid comparison to be made.

The joint distribution analyses did not take into account some significant sources of uncertainty. For example, a point estimate of 0.02807 is used to convert nominal concentrations of No. 6 fuel oil to benzene, toluene, ethylene, and xylenes (BTEX). This estimate is presumably a measure of centrality (the authors do not tell) derived from limited samples of a single fuel preparation made by a single laboratory. The authors do not indicate the possible bounds on this conversion factor. A second conversion factor was used to normalize the BTEX toxicity data to the AR_2 fraction described in the transport model. The factor used was 3, but the document states (Harwell et al. 1995; p. 108) that the factor could range from 2 to 5. Further, benzene and toluene were not included in the AR_2 fraction, despite the significant contribution toluene makes to total BTEX in bulk fuel (25%) and the fact that it is quite soluble in water (535 mg/L). The exclusion of toluene from the exposure estimation biases the analysis to underestimate risk but it is uncertain by how much. Finally, the model analyses assumed that 48% of No. 6 fuel oil is aromatics, yet the authors state that the percent aromatics have been shown to vary from 7 to 65%. Including this source of uncertainty in the joint distribution analysis could have a profound effect on the resulting distribution of quotients (this topic is listed as a research need).

In many places in the risk characterization section interesting and useful analyses were being done, but key details were often missing that made it difficult for reviewers to judge the quality of the analyses and the validity of the conclusions. Missing details were often in the supporting documentation, other times not. For example, the logistic regression analyses on the toxicity data represent a considerable improvement over derivation of no observable effects concentrations

(NOECs) and lowest observable effects concentrations (LOECs), but unfortunately goodness-of-fit statistics, confidence intervals about the mean, and prediction intervals were not provided. Without this information, it is hard to decide how confident one should be about the estimated effects and lethality concentrations.

One of the approaches used to estimate community level risks was to combine "model key species" into a "complex that represents a 'holistic' picture of the distribution and abundance of 13 key ecological resource species .... " (Harwell et al. 1995; p. 114). This complex is stated to "be a good gauge of interaction and co-occurrence." Information is needed to explain how this "complex" was calculated and how it could possibly take into account species interactions and co-occurrence. Information is not provided as to whether the exposure distributions are probability density functions or reverse cumulative distributions. Finally, discussions in Harwell et al. (1995; p. 128) indicate that expected mortalities from co-occurrence of sea trout of the recruit age class with either fuel type are expected to be very small (<0.6%). Figure V 8, however, shows that a considerable portion of the exposure distribution exceeds levels that would cause greater than 10 to 20% mortality (depending on fuel type). In the text evaluating how oil slicks in the past have affected the environment (Section V.4.5), no information is provided to determine if past spills of bunker C, light diesel have any relevance to the kinds of damage that might be expected from spills of No. 6 fuel oil.

It appears that the effects concentrations (e.g., LC_{10}-, LC_{95}-) were "multiplied by 50 to represent the associated exposure of a two-day period (comparable to the 48-hr tests)" (Harwell et al. 1995; p. 104). It is unclear why this was done. A more appropriate approach to incorporate exposure duration in the toxicity estimates would be to explicitly model the concentration-duration-response relationship or use one of the time-to-death methods discussed in chapter 4 of Newman (1995).

Portability of this Assessment to Other Sites

This charge to the reviewers evaluated the major issues to consider and applicability of this ecological risk assessment to assess impacts on ecological resources from a spill at other coastal sites.

The approach seems appropriate for application to other sites. The many issues tackled in the assessment would all need to be considered in assessments of other sites. These include identifying selected locations, spill sizes, climatological and hydrological conditions, at-risk biota, and a modification of scenario characteristics. Also, the inclusion of population models could draw more on survival time models and/or fisheries stock assessment models, etc., that together can be used to construct risk scenarios that are internally consistent and represent the range of risks posed by a future spill. Other issues to consider would be data availability, budgets for new research (e.g., toxicity studies on native biota, collection and entering of data into a GIS database), and availability of local expertise to conduct fate modeling, toxicity testing, etc.

To some extent, the assessment endpoints and measures of effect for Orimulsion 100 are transportable to assessments of other marine and estuarine sites. For example, any assessment of risks posed by an Orimulsion 100 spill in saline waters would likely focus on sensitive, pelagic biota because the bitumen particles for the most part end up in the water column. Thus, sea trout is an appropriate assessment endpoint for marine sites throughout its range. Farther north, one might choose early life stages of sea bass. Another species that could be considered for risk assessments of spills on the west coast would be salmon because juveniles have to pass through estuaries on their way out to sea. Similarly, adult salmon pass through estuaries on their way to spawning grounds. Spills in west coast estuaries during these critical times could have a significant impact on salmon populations. As with the Tampa Bay assessment, assessments at other estuarine and marine sites would not likely need to focus on emergent vegetation and other high shoreline communities because Orimulsion 100 is not deposited to this area in significant quantities.

The approach of using spatially explicit methods and sophisticated hydrodynamic fate and transport models to estimate exposures resulting from hypothetical spills is a useful one and could be used at other sites. Population modeling, toxicity testing with native species, and distributional analyses to account for uncertainties are also highly recommended for other sites. Details of how the methods are applied need to be put forward.

Fate and Transport Methods
This charge to the reviewers evaluated Orimulsion 100 density issues; exposure assumptions, transport models, and impacts of spills; and the ability of models to predict the release rate, weathering, and transport of Orimulsion 100. In addition, the scenario factors and conditions were evaluated for appropriateness.

The reports (Harwell et al. 1995, Ault et al. 1995) give excellent overviews and analyses of the buoyancy of Orimulsion 100 in different salinity waters and following weathering. The use of spatially explicit and dynamic models that account for local conditions is a state-of-the-art approach. Further, there appears to have been an extensive effort to gather the information required to parameterize these models.

An assumption is implied that only the instantaneous concentration to which an organism is exposed determines the toxic effect at any moment. "...the impact of the spill can be measured by the integral of the concentration time series of the total hydrocarbons in the water at the given critical-habitat location ...." However, there could easily be a cumulative dose effect that results in death. In that case, exposure to one concentration at time t_x could be influenced by the concentration experienced at time t_{x-1}, t_{x-2}, etc. Or, after exposure ends (time x), latent mortality could still occur at times longer than x.

The decision to focus on four locations for hypothetical spill sites and three seasonal conditions seems logical and follows from extensive consultations and early modeling efforts. The transport models chosen (and further developed) seem to be state-of-the-art and their use to investigate sensitivity of outputs to factors such as location, season, climatic conditions, wind direction, and spill size was very informative.

Preliminary studies on weathering of both fuel types (Brown et al. 1995, Chapter 4) suggest that further analysis of the persistence of medium-to-high molecular weight compounds in both fuel types would be warranted. More information is certainly needed on a larger scale (e.g., mesocosms) to better understand the weathering processes, physical and chemical fate of oil in water dispersions of the two fuel types, and the long-term fate of the two fuels.

Toxicity Test Methods
This topic evaluated whether the toxicity studies conducted were adequate to assess effects of this compound on aquatic life. Toxicity tests were evaluated for appropriate endpoints and scenarios of relevant target organisms or ecological resources most at risk from releases of Orimulsion and oil spills.

The scenarios seem to focus on the appropriate ecological entities. The toxicity studies were generally acceptable for the assessment. It might have been useful to have a bottom fish, such as the southern flounder, which was valued in the area. With the exception of benthic biota (identified as a research need), the risk scenarios addressed for waterborne exposures of Orimulsion 100 and No. 6 fuel oil were appropriate (i.e., juvenile species of fish, pelagic invertebrates). Further, the focus on risks to mangroves, sea grasses and other shoreline biota was appropriate for estimating risks of No. 6 fuel oil slicks. The Orimulsion 100 toxicity tests involving mangrove propagules and seedlings convincingly demonstrated that Orimulsion 100 poses little risk to these organisms. Perhaps the risks of Orimulsion 100 tar balls to shoreline biota should have been considered. More effort on effects on reproduction and growth would have been useful but would have been expensive and time consuming to produce. The subsequent toxicity tests did include a number of indigenous benthic species.

The toxicity studies conducted as part of this project contributed valuable information to the assessment. For example, the tests involving mangrove propagules and seedlings helped convince one reviewer that No. 6 fuel oil slick poses more of a risk to these species than does Orimulsion 100. The comparative study of toxicities of No. 6 fuel oil and Orimulsion 100 to early life stages of sea trout was particularly important given that this species was the major assessment endpoint in this project.

Results are presented in the documents (e.g., growth and production on page 5-14; page 5-20, paragraph 1 in 5.4.1. of Harwell et al. 1995) with no expression of power or minimum significant

difference. Discussions on the effects of the materials on growth and uncertainty in hypothesis tests without a statement of power or minimum significant differences are of limited use.

The analysis of the data and endpoints was inadequate for fitting the demographic models. Use of basic demographic methods (Caswell 1989, as cited in the report) or survival models (e.g., Newman 1995) would have eliminated this problem. If the LC_{50} dose response curves were used later by the modelers in a logistic model, the data should have been analyzed with logit methods. The rationale for using 48 hr LC_{50} data in a logistic model to predict an LC_{10} and then using this as a threshold of detectable/significant toxicity in simulations (which was based on acceptable criteria for control mortality in the toxicity tests, Harwell et al. 1995; p. 106) needs to be stated as a science policy decision rather than one based on ecology.

The assumption is made throughout the report that the major concern with a spill of either fuel will be the acute effects associated with water column concentrations of hydrocarbons. Given the relatively high concentrations of low molecular weight aromatic compounds associated with No. 6 fuel oil, this is a relatively sound assumption to make in a first approximation of spill conditions. The toxicity of No. 6 fuel oil is normalized to benzene, toluene, and xylene concentrations that are indeed the most toxic and the most short-lived compounds in an oil slick following a spill. Little analysis is given to the longer-term effects associated with the accumulation of higher molecular weight compounds from No. 6 fuel oil, especially in sedimentary environments, although it is acknowledged that this could occur.

Another assumption made throughout the analysis is that Orimulsion 100 will not have long-term effects on ecosystems because it does not adhere to sediment particles and is not likely to accumulate in benthic habitats. This is largely unsubstantiated by the data presented in the supporting documents. In fact the Orimulsion 100 showed a greater adhesion to sediments than No. 6 fuel oil and could under certain hydrographic conditions accumulate in benthic habitats. However, the authors of the comparative risk assessment report and subsequent studies make the case that the vertical velocities of water movement in Tampa Bay greatly exceed settling velocities of Orimulsion, including when particulate-bound, suggesting that there would not be significant settling onto the bottom or significant exposures to the benthic organisms of the Bay.

Suggested Improvements for the Tampa Bay Risk Assessment
To further address the relative risks associated with a spill of Orimulsion in Tampa Bay, there are several technical issues that could be addressed to better understand the ultimate fate and effects of Orimulsion in Tampa Bay and other coastal environments. These research needs are considered to be the responsibility of Bitor and/or users of Orimulsion (EPA 1999a).

Toxicology
Further research could verify the differences in toxicity and persistence of major hydrocarbons of concern (lower-to-higher molecular aromatic compounds, alkyl-substituted aromatics, and compounds unique to Orimulsion) between the two fuel types.

The toxicity database is not large for Orimulsion 400, especially for oil-in-water preparations. To determine the species sensitivity distribution for pelagic biota, it would be useful to test additional early life stages of marine fish species other than spotted sea trout, and invertebrates and macroalgae. The additional data would be useful in determining whether spotted sea trout is a very sensitive species.

Several of the factors used to convert the No. 6 fuel oil toxicity data so that the results were comparable to the exposure data were based on very limited information. Studies involving multiple fuel preparations and laboratories should be conducted to establish the BTEX conversion factor and the distribution around it. The appropriate distribution and parameterization for normalizing the BTEX to the AR2 fraction also need to be established. Clearly, studies need to be done to establish the percent fraction of aromatics in No. 6 fuel oil. If this fraction is highly variable, then this information needs to be incorporated in future exposure analyses.

Research on how aquatic species respond to the types of exposure expected after a spill (e.g., declining concentrations over time) rather than the constant exposures used in typical toxicity tests would provide useful information.

Benthic Community
A more in-depth analysis of the fate and effects of Orimulsion on benthic communities including more effects on invertebrates and key fish species would be of interest. This would include: weathering processes, bacterial associations, and ultimate deposition.

The potential effects, from the formation of Orimulsion tar balls at the surface of marine waters, on shoreline and tidal communities should be further evaluated in the risk characterization section.

Modeling
Use of basic demographic methods (Caswell 1989, as cited in the report) or survival models (e.g., Newman 1995) should be utilized for toxicity data. The generation of survival functions with time could then be applied to population models.

Improved prediction methods are needed for the exposure fields for both fuel types, including estimates of the exposure concentrations and persistence of medium to higher molecular weight aromatics, and alkyl-substituted aromatics of both fuel types and the surfactant components of Orimulsion.

Modeling comparisons of chemically dispersed oil, naturally dispersed oil and Orimulsion, with specific evaluation of short-term and near-field exposure regimes and long-term and far-field exposure regimes should be conducted.

The joint distribution analyses could further address significant sources of uncertainty. Including these sources of uncertainty in the joint distribution analysis could have a profound effect on the resulting distribution of quotients.

Mitigation
Although deliberately not addressed in the review, the mitigation procedures that could be used following a spill of either fuel type need to be explored in more detail to fully evaluate Orimulsion as a fuel alternative.

Assessment of Risk from Air Emissions
It was not possible in this study to conduct a complete assessment of risks associated with exposure to air pollutants from the emissions of Orimulsion combustion. However, it is possible to examine a very complete risk assessment for a similar fuel. In 1996, EPA completed a major study (referred to here as the Utility Study) of the risks to human health from emissions by electric utility steam generating units (EPA 1998). In that study, a complete inhalation exposure study was done to evaluate cancer risks associated with exposure to hazardous air pollutants (HAPs).

One of the HAPs evaluated in detail was Ni emitted from both coal- and oil-fired power plants. The study calculated the risk of cancer to a maximally exposed individual due to inhalation exposure to Ni, the number of people that would be at different levels of risk, the number of plants for which the additional cancer risk was greater than 1 in 10^6, and the total number of additional cancer cases that could be attributed to Ni exposure from power plant emissions.

The study assumed that 100% of Ni emissions were in subsulfide form, which is the most carcinogenic form of Ni; however, the dominant forms of nickel are typically the soluble salts and oxides (EPA 1998). The study notes that this is a very conservative assumption, since it is likely that other forms of Ni are also present, which would reduce the total carcinogenicity of the pollutants.

For coal-fired plants, a maximally exposed individual would face a cancer risk due to exposure to Ni from utility combustion of 1×10^{-7}, and for the U.S. as a whole, an increase of 0.02 case of cancer could be expected to be caused by exposure to utility-generated Ni emissions. This analysis does not consider long-range transport of emissions, nor does it account for exposure pathways other than

inhalation. Both of these factors would act to increase the calculated cancer risk, by a factor of up to 7 (EPA 1998). These factors may be somewhat offset by the assumption that all Ni emitted is in the subsulfide form, but in any case, Ni emissions from coal-fired power plants do not appear to form a substantial cancer risk for the U.S. population as a whole.

The situation is somewhat different for Ni emissions from oil-fired power plants. Because of the higher Ni content of heavy fuel oils and the fact that more oil-fired plants are closer to population centers than are coal-fired plants, a maximally exposed individual would face a $9x10^{-5}$ risk of cancer due to exposure to Ni emissions from oil-fired utility plants, roughly 2 orders of magnitude greater risk than for coal. The Utility Study estimated that 1.65 million people faced a cancer risk greater than $1x10^{-6}$, and that nationwide, inhalation exposure to Ni emissions from oil-fired power plants would result in an additional 0.4 cancer cases. Similar analyses were also conducted in the Utility Study for As and Cr. Similar to Ni, speciation of Cr compounds is an important factor in the toxicity of Cr compounds. The Utility Study assumed that the only risk of cancer from inhalation of Cr was due to hexavalent chromium (Cr VI) species, and that trivalent chromium (Cr III) species did not contribute to cancer risk.

The Utility Study also noted differences in reported Inhalation Unit Risk Estimate (IURE) values for As. IURE values ranged from $1.4x10^{-3}$ to $6x10^{-3}$ per µg/m^3, with the higher value representing higher risk per unit As concentration. In the Utility Study's quantification of risk, an IURE value of $4.3x10^{-3}$ per µg/m^3 was used.

Table 8-1 presents a summary of cancer risk data for exposure to HAPs reported in the Utility Study. These results indicate that the total additional cancer cases attributed to emissions from oil-fired utility boilers is 0.5. These results do not account for indirect exposure or exposure to emissions transported over long range, but do account for the conservative assumptions of 100% subsulfide forms of Ni and the mid-range value for As IURE.

One can use these results as a basis for understanding the potential risks that may result from widespread use of Orimulsion. If Orimulsion were to replace all heavy fuel oil in utility boilers, a reasonable initial estimate of cancer risk due to Ni emissions from those boilers would be to assume similar results as for heavy fuel oil, since Ni content of heavy fuel oil and Orimulsion are often very similar. In general, the Ni content of Orimulsion is likely to be slightly higher than that of heavy fuel oil. However, the majority of oil-fired plants are installed with minimum abatement equipment and therefore relative emissions of nickel from a commercially operating Orimulsion plant installed with ESPs and FGD would be orders of magnitude lower. A complete risk assessment would have to be conducted for a quantitative estimate to be made.

Since Orimulsion will be introduced incrementally and in small quantities compared to the total use of heavy fuel oil,[1] it is reasonable to consider the maximum risk calculated for exposure to heavy fuel oil HAP emissions. There were 0.4 additional incidences of cancer estimated to be caused by exposure to Ni emissions from all 137 oil-fired plants in the U.S. A reasonable initial estimate of the cancer risk associated with exposure to emissions of Ni from Orimulsion combustion would be less than the 0.4 incidences noted above. For all HAPs emitted from heavy fuel oil, the total additional incidences of cancer were estimated to be 0.5. Again, the additional incidences of cancer associated with Orimulsion combustion would be expected to be less than this.

This comparison assumes that Orimulsion is introduced incrementally over a period of years, and that the total use of Orimulsion is not a significant percentage (say more than 10%) of heavy fuel oil use. Significant increases in Orimulsion use, in terms of both number of plants and total consumption, would require a dedicated analysis to accurately estimate the risks associated with its use.

The risk assessment results presented in Table 8-1 do not include long-range transport or indirect exposure. Including either of these factors will increase the total cancer risk (EPA 1998). In addition, there are risks other than cancer that may play a role in determining the total risk to health. Exposure

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[1]Total U.S. fuel oil use is discussed in Chapter 9.

Table 8-1. Summary of risk estimates from inhalation exposure to priority HAPs for 137 oil fired utility boilers in the U.S. (EPA 1998).

Pollutant	Carcinogens				Noncarcinogen
	Highest MEI[1] Cancer Risk	Population with Risk > 10^{-6}	No. of Plants with MIR[2] > 10^{-6}	Cancer Incidence (cases/year)	Maximum HQ[3]
As	1×10^{-5}	2,400	2	0.04	NA[4]
Be	7×10^{-7}	0	0	0.002	NA
Cd	2×10^{-6}	45	1	0.005	NA
Cr	5×10^{-6}	2,300	1	0.02	NA
Dioxin/Furans	1×10^{-7}	0	0	0.0007	NA
HCl	NA	0	0	NA	0.06
Pb	NA	0	0	NA	0.004
Mn	NA	0	0	NA	0.04
Hg	NA	0	0	NA	--
Ni	9×10^{-5}	1,650,000	20	0.4	NA

1. Maximum exposed individual
2. Maximum individual risk
3. Health quotient
4. Not applicable

to $PM_{2.5}$, for instance, has been linked to increases in cardio-pulmonary disease (EPA 1996), and that issue is not addressed here.

Conclusions

Reviewers of a risk assessment of Orimulsion use in the Tampa Bay, Florida area (Harwell et al. 1995) agreed with that report's major conclusion that a spill of Orimulsion 100 likely poses a similar or lower risk to Tampa Bay biota than does an equivalent spill volume of No. 6 fuel oil. However, the reviewers noted that parts of the assessment, such as risk characterization, population modeling, and impacts to benthic communities, were identified as assessment topics that could be improved. The reviewers recommended that these improvements would enhance the Tampa Bay report, but their judgment was that the improvements would not impact the conclusions put forward by the original report. The review of the original report (Harwell et al. 1995) did not examine factors outside the scope of the Harwell study, which may have additional significant ecological or health impacts.

Emissions of Ni from the combustion of Orimulsion were compared to those from heavy fuel oil in the context of an assessment of risk associated with HAP emissions from electric utility power boilers. This comparison estimated that the cancer risk associated with exposure to emissions of Ni from Orimulsion combustion would be less than the 0.4 incidences estimated to be similar to those associated with heavy fuel oil combustion in utility steam generating units.

Chapter 9
Comparison of Orimulsion
with Other Fossil Fuels

One of the key questions regarding the environmental impact of Orimulsion use is, "How will emissions change if Orimulsion is used instead of other fossil fuels?" From the perspective of fuel reserves, Orimulsion has the potential to contribute a significant portion of U.S. energy consumption. Total recoverable Orinoco bitumen reserves have been estimated at approximately 267×10^9 bbls (oil equivalent) (U.S. Department of Energy 1998a), compared to 22.5×10^9 bbls of U.S. recoverable crude oil reserves and an energy equivalent of 995×10^9 bbls of crude oil in U.S. recoverable coal reserves (U.S. Department of Energy 1998b). The actual degree to which Orimulsion is used in the U.S. will depend upon many factors, such as relative delivered prices of different fuels and the cost of using those fuels, including environmental and other operating costs.

The most significant potential use of Orimulsion is in utility and industrial fuel combustion, where currently the most heavily used fuel is coal, followed, in order, by natural gas and fuel oil. Coal comprises approximately 83% of the fuel consumed for electricity production in the U.S. and approximately 47% of the combined utility and industrial fuel use. Natural gas is used for less than 14% of the U.S. electricity production and for just over 30% of the combined utility and industrial fuel consumption. Less than 4% of electricity is generated from the combustion of fuel oil, and just under 23% of combined utility and industrial fuel consumption is fuel oil (U.S. Department of Energy 1998b). While the most attractive opportunity for Orimulsion in the U.S. may currently be as a replacement for fuel oil due to the relative prices and the ability to use much of the existing fuel handling and storage equipment at an oil-fired facility, Orimulsion can also be used in place of coal or natural gas, as illustrated in Chapter 3 by the number of (originally) coal-fired units converted to Orimulsion.

Because nearly any use of Orimulsion would replace coal, oil, or natural gas, it is important to compare the air emissions of these fuels with Orimulsion to understand the impact Orimulsion use would have from an environmental perspective. The different properties of these fuels and the manner in which they are used are responsible for differences in pollution emissions, and the contents of impurities in these fuels play the strongest role in emissions of air pollutants.

Previous chapters have presented properties, use, and emissions of Orimulsion in considerable detail. The following discussions provide less detailed information on properties, use, and emissions associated with other fossil fuels.

Fuel Properties
Coal
There is a broad body of literature devoted to studies of the properties and characteristics of coal. While much of this work is focused on energy conversion, a significant portion of the literature addresses issues associated with air pollution from the combustion of coal. Coal contains relatively high levels of sulfur (S) compared with many other fuels. In the U.S., the sulfur content of coal ranges from less than 0.4% to greater than 2.5% (see Figure 9-1). Nearly all of the S in coal is transformed to SO_2 during combustion, resulting in a substantial level of SO_2 emissions from coal combustion. In 1995, coal combustion by utility and industrial users accounted for 13.7 million tons of the U.S. total of 18.3 million tons of SO_2 emissions (Fitz-Simons et al. 1995). The S content of coal is therefore an important factor in determining what fuel to use in a particular application.

In addition to the S content of coal, trace metal concentrations in the fuel are also of concern. Of primary concern are arsenic (As), chromium (Cr), mercury (Hg), and Ni (see Table 9-1). Swaine (1994) reports As concentrations in world coals range from 0.5 to 80 ppm, Cr from 0.5 to 50 ppm, Hg from 0.02 to 1 ppm, and Ni from 0.5 to 50 ppm. In addition, he notes that V contents range from 2 to 100 ppm and Zn from 5 to 300 ppm. Measured values of trace elements in U.S. coals
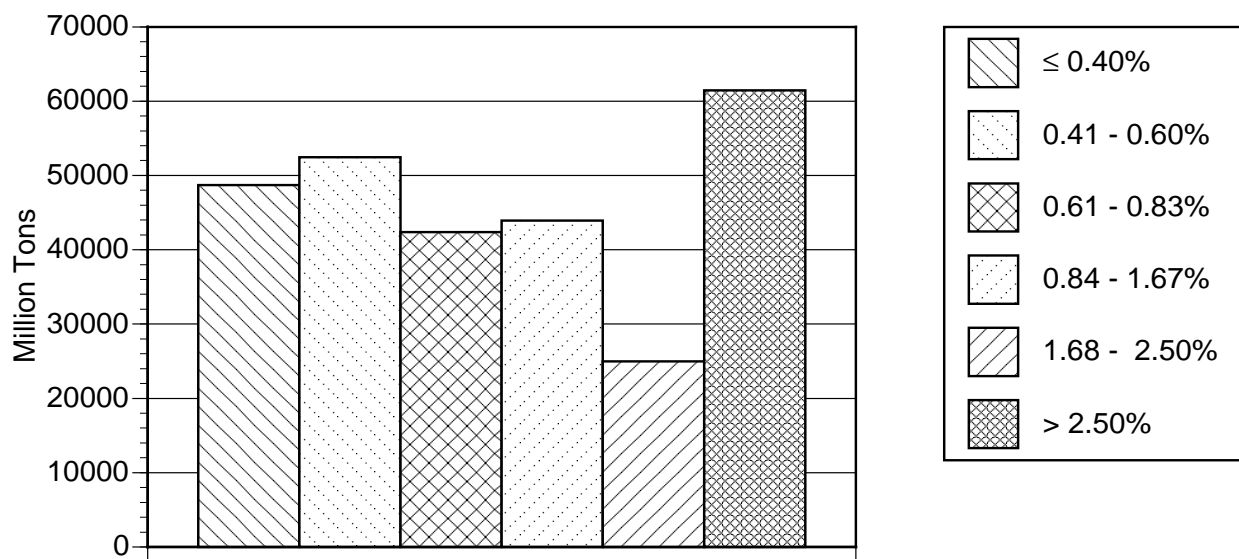
Figure 9-1. Estimated recoverable reserves of coal in the U.S. by sulfur content (U.S. Department of Energy 1997).

indicate similarly broad ranges, but average values tend to be toward the lower end of the ranges. Table 9-2 shows average values and ranges of As, Cr, Hg, and Ni contents of coals from different regions in the U.S.

Coal cleaning can reduce the amount of metals fed into a boiler or furnace. The effectiveness of cleaning processes depends strongly upon how an element is bound chemically within a coal and how the element is physically distributed throughout the coal. As much as 95% of some metals can be removed during cleaning, but in many cases, wide ranges of metal removals are reported, making it difficult to predict the effectiveness of coal cleaning (Finkelman 1994).

Elemental carbon (C) contents of U.S. coals range from just over 70% to as high as 94%, with elemental hydrogen (H) contents ranging from 4 to 11%. These values result in molar H:C ratios ranging from 0.5 to 1.7 (Babcock & Wilcox 1972).

Fuel Oil
Trace metal and S contents of fuel oils are dependent upon both the source of the crude oil and the

Table 9-1. Ranges of trace element concentrations in coals, ppm (Swaine1994).

Element	Range	Element	Range
As	0.5-80	Ni	0.5-50
Be	0.1-15	Pb	2-80
Cd	0.1-3	Sb	0.05-10
Cr	0.5-60	Se	0.2-10
Cu	0.5-50	V	2-100
Hg	0.02-1	Zn	5-300
Mn	5-300		

Table 9-2. Range of selected average trace element concentrations for U.S. coals from different regions of the country, and maximum and minimum concentrations from individual samples (Brooks 1989).

Element	Range (ppm)	Minimum (ppm)	Maximum (ppm)
As	2-27	0.5	357
Cr	5-27	< 0.5	400
Hg	0.06-4.4	< 0.01	63
Ni	3-27	< 0.5	580

extent to which refining and blending processes remove, dilute, or concentrate the elements. Crude oils contain substantially lower inorganic matter than do coals, and also significantly lower concentrations of most impurities. Due to the refining process, residual oils usually have different trace element contents than the crude oils from which they are formed, although crude oils that have high trace element content will produce residual oils that are also high in the same trace element concentrations. In addition to S, the most common trace elements in residual oils are Ni and V. Sulfur contents of selected residual oils have been reported as ranging between 0.22 and 2.44%. Residual oils from California, Indonesia, Malaysia, Pennsylvania, and Venezuela contain greater than 50 ppm of V, and the California, Pennsylvania, and Venezuela residual oils also contain greater than 50 ppm of Ni. Trace metal and S contents are not necessarily correlated. The highest S content of the reported residual oils was found in a Mexican oil, which had less than 50 ppm Ni and V, while the residual oil with the lowest reported S content (0.22%) was the Indonesian/Malaysian oil, which had 101 ppm V. Table 9-3 presents trace element concentrations of residual fuel oils used in the U.S. Residual fuel oils contain 85-87% C and 10-12% H by weight, resulting in molar H:C ratios of 1.4-1.7 (Reed 1998a).

Natural Gas

Natural gas is composed primarily of methane (CH_4), with some heavier hydrocarbons and typically small amounts of CO_2 and N_2. When extracted, natural gas may contain sulfur compounds such as hydrogen sulfide (H_2S), but these compounds are normally removed before distribution. Natural gas does not contain substantial quantities of HAPs. EPA's study of HAP emissions from electric power generating units estimated 1990 emissions of As, Cd, Cr, Pb, Hg, and Ni to total less than 4.2 tons/year from all 267 natural gas fired units in operation at the time the report was prepared (EPA 1998). Of these HAPs, the majority was estimated to be of Ni at 2.3 tons/year of total industry emissions, followed by Cr at 1.2 tons/year. Molar C:H ratios for natural gas range approximate 4 (equal to the C:H ratio for CH_4), but are in practice somewhat less due to the presence of heavier hydrocarbons such as ethane (C_2H_6) (Reed 1998b).

Table 9-3. Range of averages and reported typical values of trace element concentrations in residual fuel oils from different sources (Brooks 1989, Reed 1998a).

Element	Range (ppm)	Typical Values (ppm)
As	0.011-0.8	0.36
Cr	0.0019 - <5[1]	0.40
Hg	0.007-10	0.06
Ni	6-73	24
V	>50 - 226	Not reported

1. The upper bound of measured Cr concentrations was reported as 5 ppm, with 2 ppm as the highest reported specific value.

Fuel Use

In evaluating the potential impact of Orimulsion use in the U.S., it is important to understand the current energy use patterns that may be affected by the introduction of Orimulsion, particularly for utilities, since nearly all Orimulsion use has been as a utility fuel. In 1997, U.S. utilities generated 2.15×10^{12} kW-hrs of electricity from fossil fuels. As illustrated in Figure 9-2, the majority (83%) of this was generated from coal, with 13% from natural gas and the remaining 4% from petroleum (fuel oil). The 1997 price of these fuels ranged from an average of $1.27/$10^6$ Btu for coal to $2.88/$10^6$ Btu for petroleum, with natural gas slightly less costly at $2.76/$10^6$ Btu (U.S. Department of Energy 1998c).

Note that, based on the capacities of plants currently burning Orimulsion, the maximum level of power generation (full load for 24 hr/day, 365 days/yr) would result in just under 34,000 million kW-hr of electricity generation. This figure, representing world-wide generating capacity, is less than half the 1997 U.S. generation from petroleum, and approximately 1.5% of the total U.S. generation in 1997. No figures for fuel cost have been reported for Orimulsion.

The combination of high price and technical similarity to fuel oil makes Orimulsion more likely to replace fuel oil than either coal or natural gas in the U.S. However, there is a potential for Orimulsion to be considered as a replacement for any of these fuels. As a liquid fuel, Orimulsion is limited in its means of cost-effective transportation modes, and is most likely to be used in situations where the end-user is near a seaport or where suitable existing pipelines are available, given the expense and time required to install a pipeline. Although Orimulsion can be transferred to river barge or railroad tank cars for transport, this transfer would raise the cost of the fuel substantially compared to direct transport from ocean tanker to end-user fuel tanks. Sites with the most cost-effective potential as Orimulsion users would then most likely be situated on or very near major seaports and currently use fuel oil as their primary fuel.

Location and current fuel type are only two factors that influence the cost of conversion to Orimulsion. Other factors may include additional or upgraded pollution control equipment and/or

Million kW-hrs (percent of total)
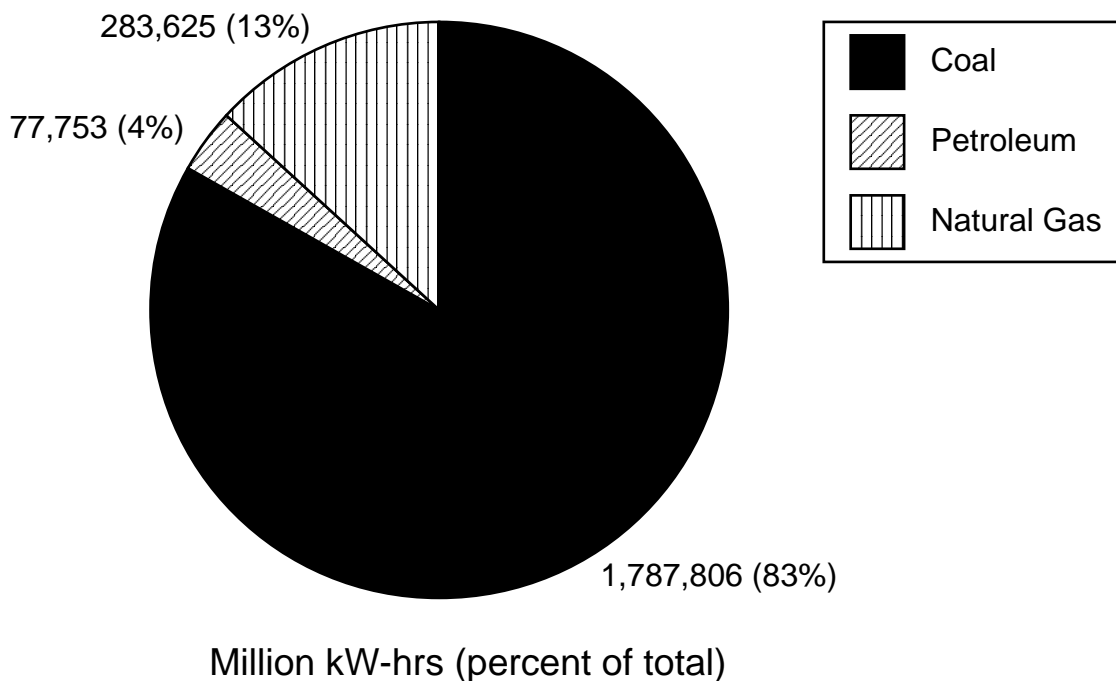
Figure 9-2. U.S. electricity generation in 1997 by fossil fuel (U.S. Department of Energy 1998c).

improvements to the plant control system. Over the long term, the largest impact on cost effectiveness will most likely be the differential cost of the two fuels. Even though conversion of oil-fired plants near seaports may be the most likely scenario in the near term, it is worthwhile to examine the pattern of fuel consumption for all three fossil fuels.

Coal

Coal is the primary fuel for utilities, with a much smaller amount directly burned for industrial energy (this section is concerned only with "steam coal" and not with metallurgical coal). In 1997, Texas used more coal than any other state, at just over 100 million tons. Roughly 95 million tons of this was used for power generation by utilities. The next 9 highest coal consumers in 1997 were Indiana, Ohio, Pennsylvania, Illinois, Kentucky, Missouri, West Virginia, Michigan, and Alabama (U.S. Department of Energy 1997). These top 10 coal consumers account for over 50% of the total U.S. consumption by utility and industrial users (see Figure 9-3). While Indiana, Ohio, Illinois, and Michigan have access to seaports on the Great Lakes and Pennsylvania has a major seaport at Philadelphia, for the most part the coal use is located away from these areas and along the Ohio River. Kentucky, Missouri, and West Virginia have water transport only via river. Alabama does have ocean access at Mobile, but again, the majority of coal use is farther inland and would require an additional form of transport if Orimulsion were to be used at an existing utility plant in the state.

Substantial replacement of coal by Orimulsion does not appear likely, based on the low price of coal relative to fuel oil and natural gas and the location of utility and industrial plants away from major seaports. That is not to say that Orimulsion cannot displace coal in individual situations. Florida, for instance, used over 20 million tons of coal in utility and industrial applications in 1997, and has several plants located at or near seaports where Orimulsion transport would be economically feasible.

Fuel Oil

U.S. fuel oil consumption by utility, industrial (including use by oil companies), and commercial sectors is shown in Figure 9-4.* Fuel oil consumption for electric power generation is substantially lower than was the case for coal, as illustrated in Figure 9-2, and is geographically distributed differently than coal. Approximately 50% of fuel oil use occurs in only 3 states: Florida, New York, and Massachusetts. A total of 75% of U.S. fuel oil consumption occurs in only 8 states - the top 3 plus Connecticut, Hawaii, Maine, North Carolina, and Pennsylvania. The majority of this consumption is for utility power generation, although little or no fuel oil is used by utilities in Maine, North Carolina, or Pennsylvania. In contrast with coal, all of the top 15 fuel oil-consuming states have access to seaports. Pennsylvania is the only state in the top 10 consumers of both coal and fuel oil, and is a producer of both fuels. Also in contrast to coal, the top 7 fuel oil-consuming states produce little or no oil, where the top coal consuming states are also coal producers (U.S. Department of Energy 1998d).

Orimulsion may have significantly greater potential to replace fuel oil than coal or natural gas due to two factors (not associated with plant configuration or hardware). First, the cost of fuel oil is higher than coal (U.S. Department of Energy 1998c). Second, the location of the major oil-consuming states along coast lines makes transport of Orimulsion less expensive. Finally, since Orimulsion handles and burns similarly to fuel oil, the technical issues surrounding conversion from fuel oil to Orimulsion are less difficult to overcome than similar conversions from coal or natural gas.

The greatest potential for Orimulsion use appears to be in areas where there is significant fuel oil usage, since these areas (in the U.S.) tend to have good access to seaports. Florida, Massachusetts, Connecticut, and Hawaii appear to have the largest potential for Orimulsion use (New York is not included here as most of the power-generating capacity is located away from direct access to seaports).

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*Residential fuel oil consumption is not considered here as it is not likely to be targeted as a potential Orimulsion market in the short term.
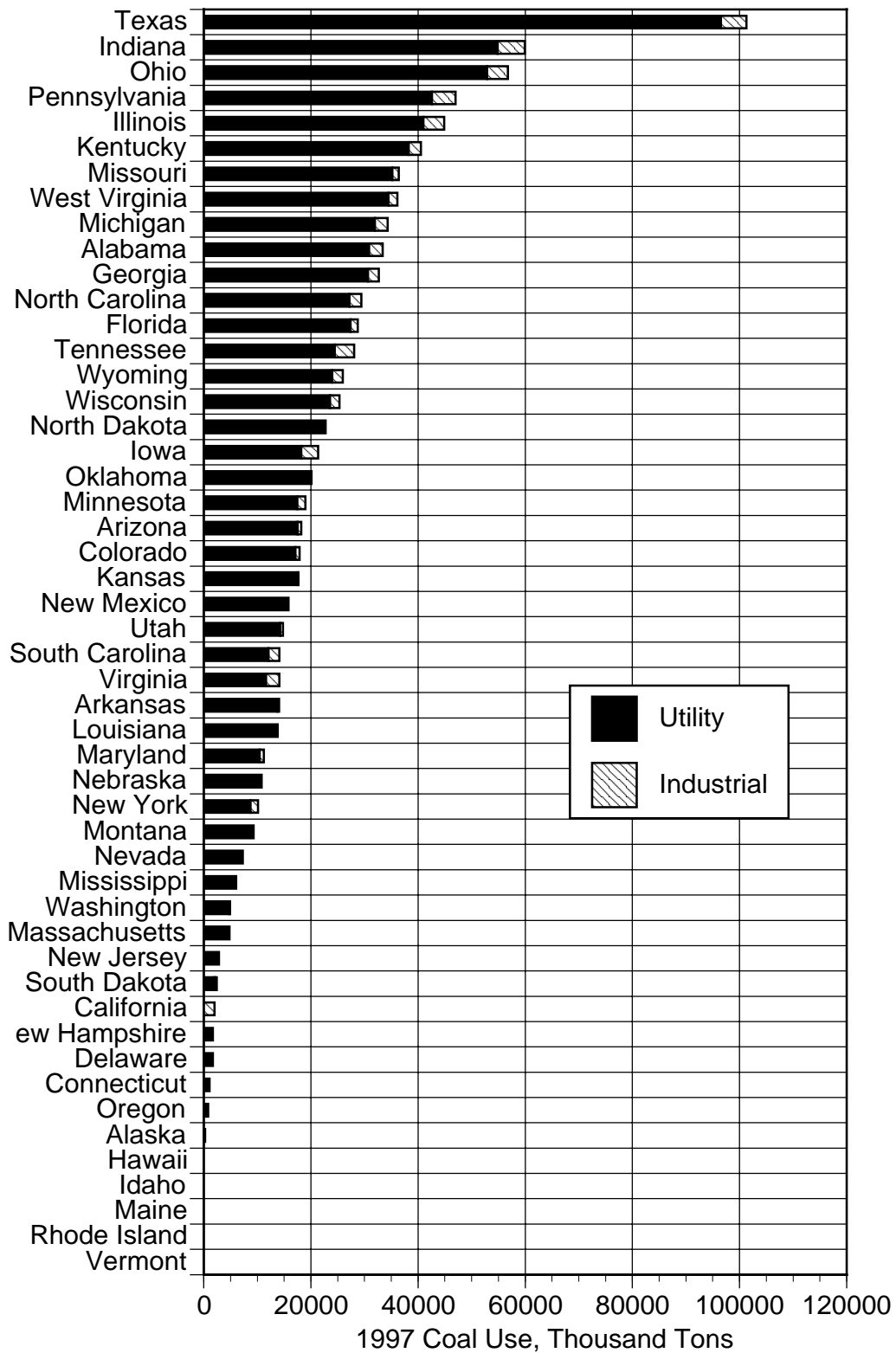
Figure 9-3. U.S. utility and industrial coal consumption in 1997 by state (U.S. Department of Energy 1997).
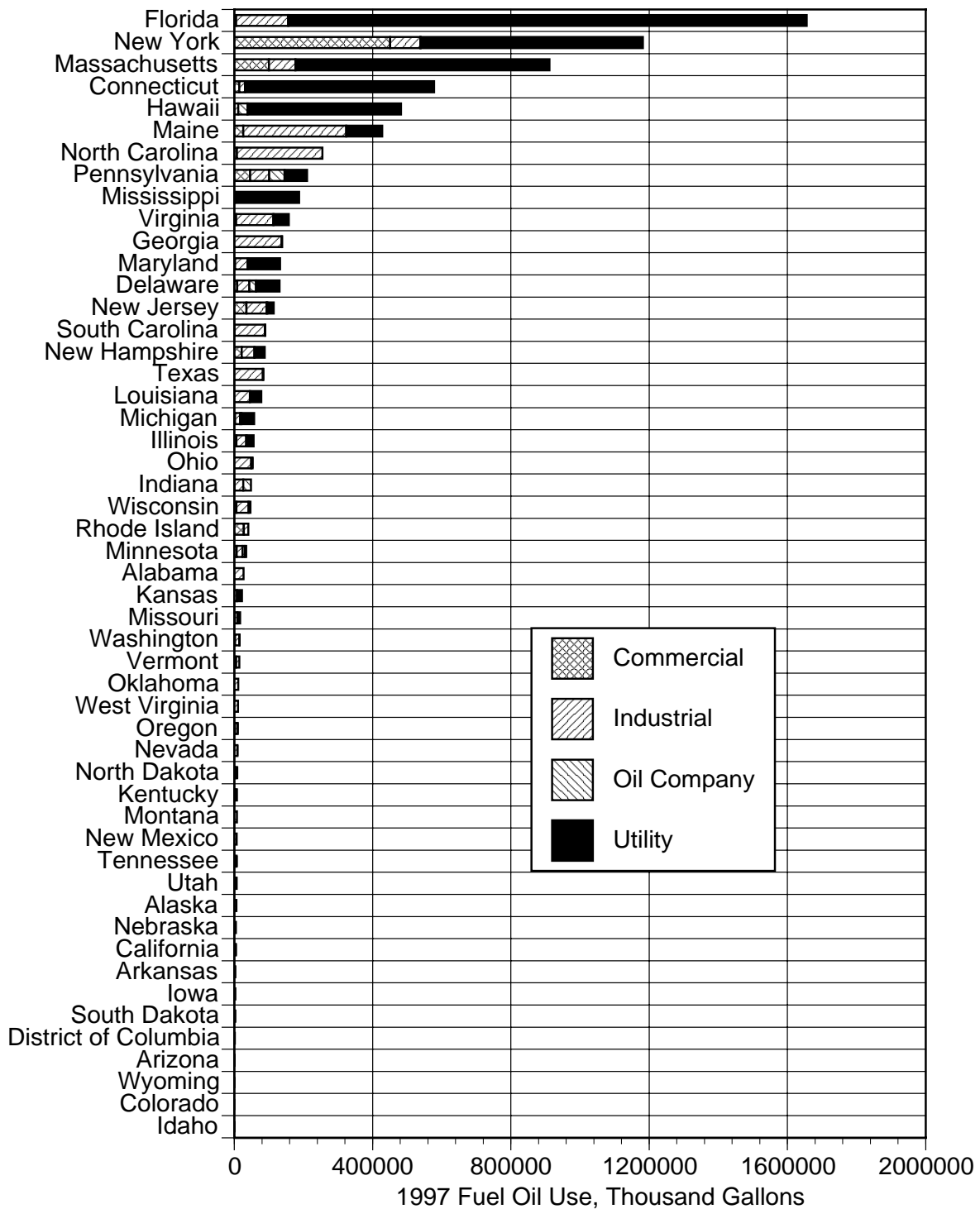
Figure 9-4. U.S. fuel oil consumption by the commercial, industrial, oil company, and utility sectors in 1997 by state (U.S. Department of Energy 1998d).

However, it should be noted that, in many conversions, Orimulsion has replaced coal as the primary fuel. Table 3-2 shows that, of the 13 boilers converted to Orimulsion, 4 were converted from pulverized coal and 3 more from a combination of pulverized coal and heavy fuel oil. The remaining six conversions were from heavy fuel oil to Orimulsion. Plants burning pulverized coal almost always have the equipment necessary to control both SO_2 and PM, potentially making the conversion from coal to Orimulsion more cost-effective than from heavy fuel oil to Orimulsion. However, the presence of existing pollution control equipment must be balanced with the potential need to install fuel storage tanks and handling systems and the possible need to upgrade or modify the pollution control equipment. In some cases, modifications to boiler components may also be needed.

Natural Gas

Natural gas consumption in the U.S. commercial, industrial, and utility sectors was highest in Texas in 1997, followed by California, Louisiana, and New York (see Figure 9-5). Texas and Louisiana are also major natural gas producers. Unlike either coal or fuel oil, natural gas is used primarily in non-utility sectors.[*] Natural gas consumption is distributed more evenly among coastal and inland states than is the case for either coal (largely inland) or fuel oil (mostly coastal) (U.S. Department of Energy 1998e). The ability to handle and burn natural gas without heating or pumping, or the need for compressed air or steam for atomizing the fuel, make natural gas more attractive as a combustion fuel compared to either fuel oil or Orimulsion. Even given the high cost of natural gas, its ease of use makes it a preferred fuel for industrial applications. There have been no reported conversions of utility plants from natural gas to Orimulsion.

Air Pollutant Emissions and Control

Emissions of air pollutants vary significantly with fuel and with combustion system design. Even for a given type of fuel, there may be substantial variation in air pollutant emissions from a single plant, due to changes in fuel properties. Both coal and heavy fuel oils vary widely in sulfur and trace element content, resulting in differences in emissions of SO_2 and metals. Differences in the amount of volatile matter in coal can impact emissions of CO, NO_x, and unburned carbon, since such differences affect the ease of fuel burnout. The design of the furnace and burners and the combustion conditions used also affect emissions of CO, NO_x, and unburned carbon, but have less influence on total emissions of PM, SO_2, and trace metals, although PM mass emissions can be strongly influenced by the amount of unburned carbon, particularly for heavy oils.

CO Emissions and Control

CO emissions from the combustion of fossil fuels can vary widely, since they are largely the result of the conditions under which combustion occurs. The major factor in determining CO emissions is the level of excess air in the boiler or furnace. CO emissions are often less than 10 ppm for natural gas combustion systems, but may be higher than 1000 ppm under low excess air conditions. Nearly all combustion systems exhibit a rapid and substantial increase in CO below a certain O_2 level. This point is often termed the "CO knee," and will vary from one unit to another. CO emissions can also increase during transient changes in load or fuel feed, as the air:fuel ratio in a single burner drops below a critical point. Smaller units and units burning less volatile fuels tend to have higher CO emissions than do larger units and units burning volatile fuels. Thus, a large natural-gas-fired boiler will be expected to emit lower concentrations of CO than a small boiler burning either coal or heavy fuel oil.

The values of CO emission rates from the combustion of bituminous coal, fuel oil, and natural gas in boilers from EPA's AP-42 are given in Table 9-4 (EPA 1995) for purposes of comparison. These values compare to emission factors from EPA's pilot-scale tests of 0.008 lb/10[6] Btu for Orimulsion 100 and No. 6 fuel oil and 0.010 lb/10[6] Btu for Orimulsion 400, all below the values given for other

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[*] As was the case for fuel oil, there is a significant residential consumption of natural gas, but the residential sector is not likely to be targeted as a potential Orimulsion market.

fossil fuels in Table 9-4.

Combustion air control is the most common method used to control CO. As combustion air levels (measured by the O_2 level in the stack or furnace combustion gases) increase, CO decreases. Alternatively, decreasing O_2 results in increased CO. This behavior holds for coal, oil, natural gas, and Orimulsion. Field tests of Orimulsion indicated CO would either decrease or stay relatively steady (see Table 3-9), and pilot-scale tests conducted prior to EPA's study also indicated either minor decreases or modest increases in CO emissions compared to the baseline fuel (usually heavy fuel oil). The results of the EPA pilot-scale tests indicate that CO emissions increased slightly when using Orimulsion 100 and Orimulsion 400 compared to those from a No. 6 fuel oil. However, optimization of the pilot-scale unit was not done, which would have likely reduced CO emissions from Orimulsion compared to the reported values.

In general, there is no evidence that would indicate that CO emissions from Orimulsion are substantially different than those from heavy fuel oil. CO emissions from coal are likely to be slightly higher, and those from natural gas slightly lower than CO emissions from the combustion of Orimulsion. For all fuels, CO emissions can be minimized by proper maintenance and operation of the combustion system to ensure steady and accurately controlled fuel and air flows through each burner.

NO_x Emissions and Control

NO_x emissions, like CO emissions, depend upon a number of factors including fuel and combustion system type, operating conditions, and the amount of nitrogen in the fuel. Advances in combustion system design (particularly burners) have resulted in significant decreases in NO_x emissions per unit heat input. NO_x emissions vary significantly with combustion conditions and burner and boiler design due to the strong influence of temperature and air/fuel mixing on NO_x formation.

For coal, NO_x emissions depend upon both the boiler and burner designs as well as the type of coal fired. For bituminous coals, uncontrolled NO_x emission rates range from 0.25 lb/10^6 Btu for arch-fired boilers to greater than 2.0 lb/10^6 Btu for wall-fired wet bottom boilers. The majority of boilers in the U.S. are either wall- or tangentially-fired designs. Tangentially-fired boilers have uncontrolled emission rates between 0.4 and 0.7 lb/10^6 Btu, while wall-fired dry bottom boilers typically have uncontrolled NO_x emission rates between 0.7 and 1.0 lb/10^6 Btu (Muzio and Quartucy 1997). Application of low NO_x combustion technology (typically burners) can reduce these emissions by 50% or more.

Uncontrolled NO_x concentrations from wall-fired dry bottom boilers firing coal are on the order of 600 ppm, while emissions from heavy fuel oil firing are roughly 250-300 ppm, and about 150 ppm for natural-gas-fired units, all corrected to 3% O_2 (Bowman 1992). These values compare to emissions from Orimulsion 100 ranging between 150 and 400 ppm and from Orimulsion 400 ranging from 80 to 160 ppm, as reported in Chapter 3.

Table 9-4. CO emission factors for coal, fuel oil, and natural gas (EPA 1995).

| Fuel	Emission Factor (lb/10^6 Btu)
Bituminous coal (pulverized coal and cyclone boilers)	0.019
Fuel oil (except for No. 2 or distillate fuel oil)	0.033
Natural gas	0.082
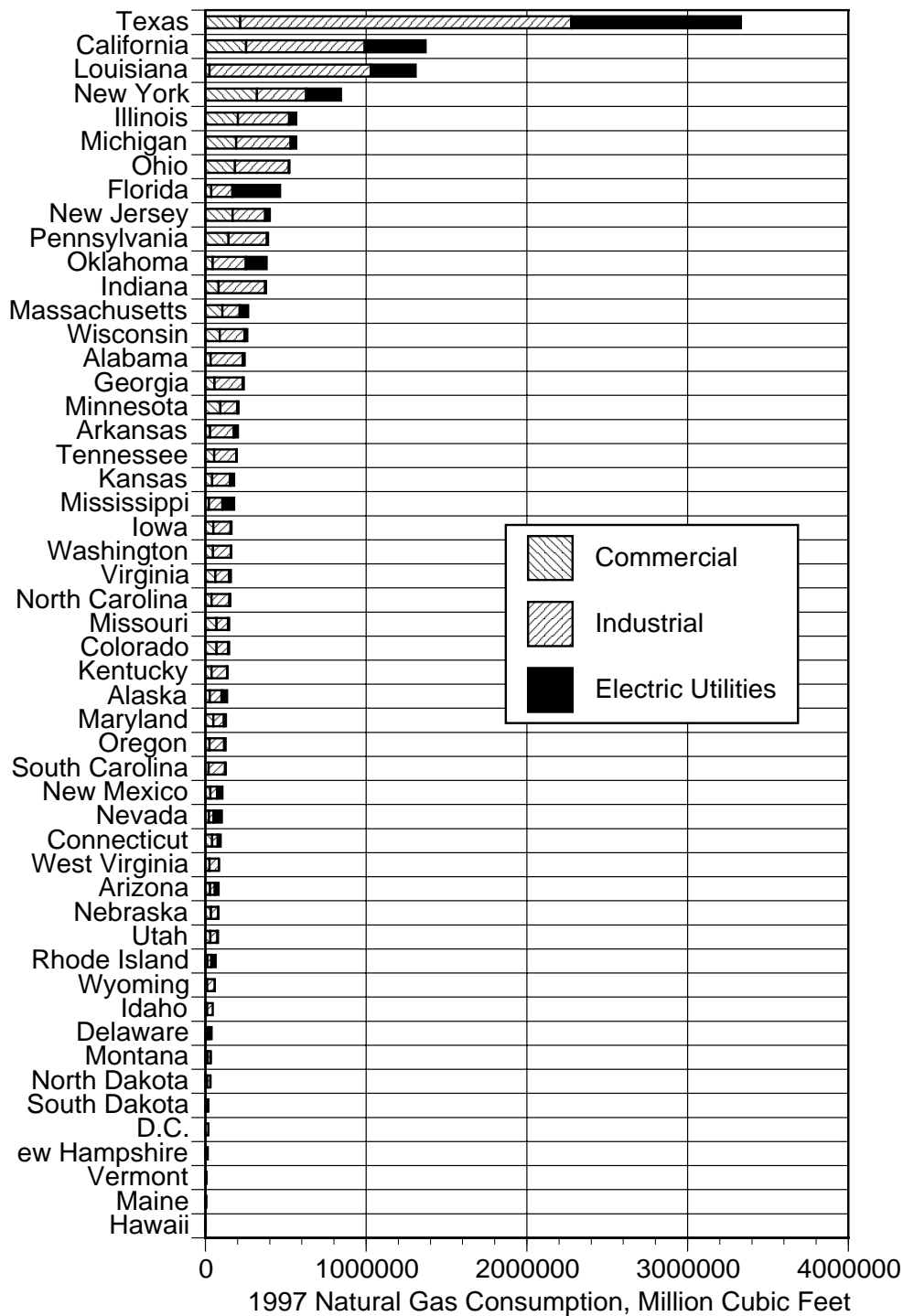
Figure 9-5. U.S. natural gas consumption by the commercial, industrial, and utility sectors in 1997 by state (U.S. Department of Energy 1998e).

Emission factors for bituminous coal range between 0.20 lb/10^6 Btu when fired in NSPS[*] tangentially-fired boilers to 0.92 lb/10^6 Btu for cyclone furnaces. For No. 6 fuel oil, AP-42 lists NO_x emission factors between a low of 0.28 lb/10^6 Btu for tangentially-fired boiler to a high of 0.45 lb/10^6 Btu for utility boilers under "normal firing." Uncontrolled NO_x emission rates for natural gas are listed as between a low of 0.17 lb/10^6 Btu for tangentially-fired boilers to a high of 0.28 lb/10^6 Btu for pre-NSPS wall-fired boilers. Controlled NO_x emissions when firing natural gas range between 0.075 lb/10^6 Btu for tangentially-fired boilers with flue gas recirculation to 0.98 lb/10^6 Btu for wall-fired boilers using low NO_x burners (LNBs) (EPA 1995). These values compare to NO_x emission factors measured during EPA's pilot-scale tests of 0.46 lb/10^6 Btu for Orimulsion 100, 0.468 lb/10^6 Btu for Orimulsion 400, and 0.542 lb/10^6 Btu for No. 6 fuel oil.

Uncontrolled NO_x emissions from Orimulsion combustion appear to be slightly lower than those reported for heavy fuel oil, although there are instances where NO_x emissions have increased when burning Orimulsion compared to heavy fuel oil (Osaka No. 4, for instance, in Table 3-10). NO_x emissions from Orimulsion are in general lower than those from coal and higher than those from natural gas.

Like CO, NO_x formation depends upon the combustion conditions, and can be minimized through optimization of the combustion system and parameters. The pilot-scale work of de Santis et al. (1996) in particular demonstrates that NO_x from Orimulsion combustion can be controlled using the conventional methods of controlled air/fuel mixing that are the basis of current LNB designs (Muzio and Quartucy 1997). Results of full-scale tests also show that staged combustion principles developed for use in reducing NO_x from coal, fuel oil, and natural gas can be effectively applied to NO_x reductions when burning Orimulsion.

Reburning technology developed for NO_x reduction at plants burning coal and fuel oil has been demonstrated as also reducing NO_x emissions when burning Orimulsion. Although much of the previously reported work centers on the use of Orimulsion as the reburning fuel, the fact that conventional combustion modification techniques can be applied to Orimulsion and its success as a reburning fuel demonstrate that plants burning Orimulsion can expect to achieve NO_x reductions with appropriately designed reburning systems in the same manner, and at approximately the same reduction level, as plants firing other fossil fuels as a primary fuel.

The experience at Osaka Unit 4 demonstrates that selective catalytic reduction (SCR) can also be used to reduce NO_x emissions from Orimulsion-fired plants. There are issues associated with other flue gas constituents, primarily SO_3, that complicate the use of SCR. The injection of NH_3 or urea can result in high levels of bisulfate particles being formed, which will substantially increase the particulate loading of the particle control equipment. Nevertheless, if adequate capacity is designed into the particle control equipment, SCR is effective in reducing NO_x emissions to a degree similar to reductions when other fossil fuels are used.

There has not been any reported use of selective noncatalytic reduction (SNCR) when using Orimulsion. Similar increases in particle loading from the formation of sulfates as noted when applying SCR would be expected when using SNCR, since both technologies rely on injection of NH_3-based compounds. Fundamentally, one would expect that SNCR would reduce NO_x to a level similar to other fossil fuels if adequate reagent is used.

SO_x Emissions and Control

SO_2 emissions are almost entirely dependent upon the amount of sulfur in the fuel. Thus, for fuels such as Orimulsion that contain relatively high sulfur, one would expect high uncontrolled SO_2

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[*]New Source Performance Standards (NSPS) were implemented for NO_x control through design of boilers in 1977. Because these standards resulted in significant changes to boiler designs, boilers built before 1977 are referred to as "pre-NSPS" and those built after 1977 as "NSPS" or "post-NSPS."

emissions. As discussed in the above section on fuel properties (and as seen in Figure 9-1), there is a broad range of sulfur contents in coal and fuel oil, making it difficult to make general statements comparing SO_2 emissions from Orimulsion to those from other fossil fuels. However, since the sulfur content of Orimulsion is similar to the upper range of sulfur contents for coal and oil, uncontrolled SO_2 emissions from Orimulsion would be expected to be in the upper range of those from fossil fuels in general.

AP-42 emission factors for SO_2 are given in terms of sulfur content for coal and fuel oils, and are noted as being in trace quantities in natural gas (EPA 1995). Table 9-5 presents emission factors for bituminous, sub-bituminous, and anthracite coal and for No. 6 fuel oil as listed in AP-42, and assuming a 2% sulfur content for each of the listed fuels. These values compare to those measured in EPA's pilot-scale tests of 0.85 lb/10^6 Btu for Orimulsion 100, 0.93 lb/10^6 Btu for Orimulsion 400, and 1.02 lb/10^6 Btu for No. 6 fuel oil.

SO_3 emissions depend upon the sulfur content as well as upon presence of other elements, notably V or Mg, that can impact the rate of SO_3 formation from SO_2 at the temperature and flue gas composition of the system. Since fuel oil tends to contain substantially more V than coal, SO_3 is typically considered to be more likely to be emitted from fuel oil combustion than from the combustion of coal. As for SO_2, SO_3 emission factors are based upon the sulfur content of the fuel oil. For No. 6 fuel oil, the listed SO_3 emission factor (in lb/10^6 Btu) is 0.038S, where S is the percent sulfur in the fuel* (EPA 1995). Full-scale experience reported for Orimulsion 100 firing lists a range of SO_3 emissions from 1 to 68 ppm, with 3 of 4 test programs reporting emissions less than 15 ppm (see Table 3-11), and recent results for Orimulsion 400 are reported as 1 ppm SO_3 at between 2 and 2.5% O_2 in the stack (Gibb 1999).

Control of SO_2 is the same for Orimulsion as for other fossil fuels, since there are no characteristics of Orimulsion combustion gases that would substantially interfere with the chemistry of conventional post-combustion SO_2 control technologies. Reductions in SO_2 emissions of 95% using a conventional limestone scrubber have been reported for full-scale operations during Orimulsion firing (SK Energy undated). SO_3 emissions control is somewhat more difficult, and may require installation of specialized equipment such as a wet ESP to adequately reduce emissions. A more common approach is that taken by several plants to minimize stack O_2 levels. This may result in problems maintaining CO levels at adequately low levels, but will help in minimizing NO_x.

In general, control of SO_2 emissions from the combustion of Orimulsion does not appear to present any significant technical difficulties beyond those normally associated with SO_2 removal for other fossil fuels. Likewise, controlling SO_3 emissions from Orimulsion combustion has been shown to be a problem that can be addressed using conventional techniques developed for other fossil fuels.

Table 9-5. SO_2 emission factors (uncontrolled) for three coal types and for No. 6 fuel oil (EPA 1995).

Fuel	Emission Factor, lb/10^6 Btu	Emission Factor for 2% S Fuel, lb/10^6 Btu
Bituminous coal	1.46S[1]	2.92
Sub-bituminous coal	1.35S	2.70
Anthracite coal	1.50S	3.00
No. 6 fuel oil	1.047S	2.09

1. S = % sulfur content of the fuel (for a 2% sulfur fuel, multiply by 2).

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*For a 1.5% sulfur oil, the emission factor would be calculated as 5.7 x 1.5 to give the estimated SO_3 emissions in lb/10^6 Btu.

PM Emissions and Control

PM emissions from the combustion of fossil fuels depend upon the amount of inorganic material in the fuel and on the effectiveness of the combustion system to fully convert the available carbon to CO_2. For coal, the primary factor in determining PM emission rates is the amount of ash in the coal. Likewise for oil, the level of inorganic matter in the fuel plays a major role in the rate of PM emissions, although the rate of PM emissions from fuel oil is more strongly influenced by the level of carbon burnout than is the case for coal, primarily because the inorganic material in fuel oils are significantly lower than in coals.

Ash levels in U.S. coals range from about 6% to as much as 30% by as-found mass (Keppler 1998), while residual oils have significantly lower ash contents, ranging from ash-free (<0.001%) to 0.2% by weight (Reed 1998a). Natural gas has no mineral matter of consequence (Reed 1998b). PM emission levels are determined by both the ash content and the level of carbon that is not consumed in the combustion process. The unburned carbon is usually a consequence of low temperatures and/or inadequate combustion O_2, and can make up a majority of the PM emitted from certain combustion system designs. Poor carbon burnout can increase PM emissions by a factor of 10 or more when burning a heavy fuel oil, compared to calculated values based on the fuel ash content. PM from natural gas combustion is usually considered to be the consequence of soot formation in high temperature, low O_2 regions of the combustor. The presence of sulfur can also contribute to PM emissions, particularly for heavy fuel oil or natural gas through formation of sulfate compounds or SO_3 droplets, making the PM emissions also dependent upon the sulfur content of the fuel.

PM emission factors for coal are given by AP-42 in terms of the coal ash content and combustion system design. Dry bottom boilers will tend to emit more PM than wet bottom and cyclone boilers, since a portion of the mineral matter is drawn off as liquid slag in the latter two types of units. Table 9-6 presents uncontrolled emission factors for different coal types and coal combustion systems, for the fuel types listed in general and for the same fuels assumed to contain 10% ash (for coals) and 1.5% sulfur (for fuel oils).

Three emission factors have been reported for previous tests of Orimulsion, two for full-scale tests and one for a pilot-scale test. The full-scale tests (during testing at Dalhousie and at the Florida

Table 9-6. Filterable PM emission factors (no controls) for different fuels and different combustion system designs (EPA 1995).

Fuel/Boiler Type	Emission Factor, lb/10^6 Btu	Emission Factor, lb/10^6 Btu (10% ash in coal or 1.5% S in fuel oil)
Bituminous, sub-bituminous, or anthracite coal/Dry bottom PC[1] boilers	0.385A[2]	3.85
Bituminous, sub-bituminous, or anthracite coal/Wet bottom PC boilers	0.269A	2.69
Bituminous coal/Cyclone furnaces	0.077A	0.77
No. 6 Fuel oil/All boiler types	0.061(S)+0.021[3]	0.11
Natural gas/All boiler types	0.002[4]	0.002

1. Pulverized coal
2. Percent ash in coal (A = 10 for 10% ash in coal)
3. Percent sulfur in oil (S = 1.5 for 1.5% sulfur in coal)
4. Filterable PM. Condensable PM = 0.006 lb/10^6 Btu

Power & Light Sanford Plant) reported PM emission factors of 0.22 and 0.17 lb/10[6] Btu, respectively (Janati 1997, Entropy 1991). The pilot-scale test (at PowerGen) reported a PM emission factor of 0.30-0.35 for No. 6 fuel oil, but less than those for pulverized bituminous coal. Emission factors measured lb/10[6] Btu (Allen and Beal 1996). Both these emission factors are higher than those given in Table 9-6 during EPA's pilot-scale testing: 0.69 lb/10[6] Btu for Orimulsion 100 and 0.75 lb/10[6] Btu for Orimulsion 400. These values compare to 0.82 lb/10[6] Btu for No. 6 fuel oil, which is substantially higher than the emission factor reported in AP-42.

Particle size distributions are an area where there does appear to be significant differences between different fossil fuels. PM generated by the combustion of pulverized coal is dominated by particles larger than 1 μm in diameter (the coarse fraction). As much as 95% of the total PM mass may be in the coarse fraction, with the remainder in the fine fraction (less than 1 μm in diameter) (Linak and Wendt 1994). On the other hand, PM generated by the combustion of heavy fuel oil tends to be almost entirely (80% or more) in the fine fraction (Hersh et al. 1979, Piper and Nazimowitz 1985, Walsh et al. 1991), although there may be some larger particles that are the consequence of incomplete oil droplet burnout (Miller et al. 1998a). Natural gas does not contain significant amounts of inorganic or solid matter, resulting in very low (and often undetectable) levels of PM emissions.

Recent editions of AP-42 (EPA 1995) have included emission rates of particles 10 μm in diameter and smaller (PM_{10}) and particles 2.5 μm in diameter and smaller ($PM_{2.5}$). For bituminous, sub-bituminous, and anthracite coal, AP-42 reports uncontrolled emissions of $PM_{2.5}$ as being 6% of the total mass, with only 2% of the total mass being smaller than 1 μm in diameter. For residual fuel oil, AP-42 lists $PM_{2.5}$ as being 52% of the total uncontrolled PM mass emitted, and 39% being smaller than 1 μm in diameter.

Full-scale tests of Orimulsion combustion reported 80 to 97% of the total PM mass as being smaller than 1 μm in diameter, and 98 to 100% of the total PM mass as PM_{10} (see Table 3-13). PM from fuel oil combustion in one of the units reporting Orimulsion results reported PM smaller than 1 μm in diameter as being 45% of the total mass, and 75% of the total mass being PM_{10}.

These values compare to approximately 90% of the total mass of PM from Orimulsion combustion being $PM_{2.5}$ and 80% smaller than 1 μm in diameter in the EPA pilot-scale tests. $PM_{2.5}$ from fuel oil combustion in these tests accounted for just over 40% of the total mass, with about 30% of the total PM mass being smaller than 1 μm in diameter. Note that a coal with 10% ash and 6% of the PM mass as $PM_{2.5}$ will have an uncontrolled $PM_{2.5}$ emission factor of 0.23 lb/10[6] Btu, comparable to the total PM emission factors for Orimulsion measured at Dalhousie and Sanford (0.22 and 0.17 lb/10[6] Btu, respectively).

Electrostatic precipitators (ESPs) are the most common form of PM control for utility applications. For industrial applications, other PM control equipment may be used, including fabric filters, wet scrubbers, or multiple cyclones. Each of these systems have collection efficiencies that are affected by particle size. Markowski et al. (1980) compared size distributions of PM from the combustion of pulverized coal, and showed that the mass of particles smaller than 1 μm was approximately equal to the mass of particles larger than 1 μm downstream of an ESP (i.e., each fraction accounts for approximately 50% of the total mass - see Figure 9-6). This is in contrast to the uncontrolled size distribution, in which as much as 95% of the total mass is in particles larger than 1 μm in diameter. This means that the collection efficiency of the smaller particles is significantly less than that of the larger particles. Note that the data shown in Figure 9-6 indicate that the total mass of particles smaller than 1 μm is substantially reduced, but not to the same degree as those of larger size.

Data for ESP control of residual oil PM included in AP-42 indicate that although $PM_{2.5}$ is controlled to a higher degree than larger particles, the difference is slight. In general, one would expect particles in the size range 0.1 - 1 μm in diameter to have lower collection efficiencies than either smaller or larger particles, based on aerosol behavior mechanisms. The lower collection efficiency for smaller
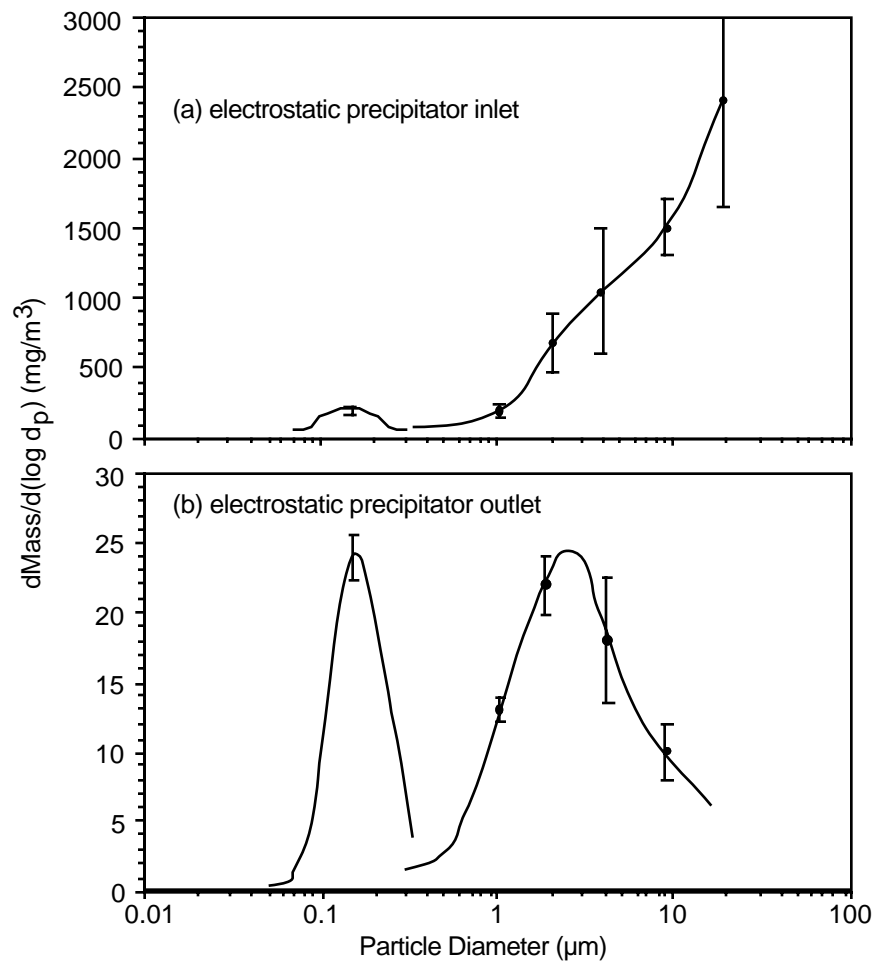
Figure 9-6. Comparison of particle size distributions from the combustion of pulverized coal before and after an ESP, with data from Markowski et al. (1980) (Linak and Wendt 1994).

particles is also evident in the AP-42 emission factor data for residual fuel oil controlled by wet scrubbers. In this case, $PM_{2.5}$ accounts for 52% of uncontrolled mass emissions, but 97% of controlled mass emissions. While the scrubber removes 94% of the total mass, it removes 89% of $PM_{2.5}$ and 99.8% of the mass larger than 2.5 μm in diameter.

Recent data for Orimulsion 400 do not agree with the above comments that small particles are removed at a lower efficiency than the larger particles. Data from Gibb (1999) show removal efficiencies of 98.4% for $PM_{2.5}$ and 91.2% for particles larger than 2.5 μm in diameter. However, the author notes that there was likely to be some re-entrainment of larger particles during rapping operations in the ESP, which may account for the lower apparent collection efficiency for the larger particles.

In general, ESPs appear to be able to adequately reduce PM emissions from the firing of Orimulsion. As discussed in Chapter 3, the ESP at Asnaes Unit 5 collected an average of 96.7% of the PM entering the ESP, although the overall drop in PM concentration (ESP inlet to stack) was just over 96%, probably due to the entrainment of droplets as the flue gas passed through the wet scrubber. ESP designs must account for the change in flue gas volumetric flow rate for such levels of particle removal to be consistently attained. The high level of water in Orimulsion significantly increases the total volumetric gas flow, which will result in increased gas velocities through the ESP. In addition,

there have been reports of increased furnace exit gas temperatures when using Orimulsion, which can also lead to higher flue gas volumes, even at steady mass flow rates (Biede et al. 1997, Meisingset et al. 1997). A further consideration is the use of NH_3-based NO_x removal technologies, which can significantly increase the particle loading upstream of PM removal equipment. Modifications such as those described in Chapter 3 at the Kashima-Kita plant may be required to address these issues, but have been shown to result in stack emissions of 20 mg/Nm^3, compared to inlet concentrations of 550-600 mg/Nm^3. Although there is limited data for capture of PM from Orimulsion using fabric filter systems, the characteristics of the particles do not appear to make use of such systems unable to adequately capture PM from Orimulsion. The pilot-scale tests of a fabric filter system did, however, note that use of a sorbent material may be required to ensure adequate filter life due to the higher levels of SO_3 present in the gas. Nevertheless, conventional technologies are able to adequately control PM from the combustion of Orimulsion, with proper design and operation.

The particle size distribution for Orimulsion PM may be more closely compared to that for a water-in-oil emulsion. Tests were conducted at EPA in 1995 on an emulsified No. 6 fuel oil to evaluate the emissions of HAPs from a No. 6 fuel oil and from the same No. 6 fuel oil emulsified with approximately 10% water (Miller 1996). Particle size distributions were also measured during those tests, and can be compared to the size distributions measured during Orimulsion firing. The 1995 tests were conducted in a Scotch marine type firetube boiler, which has much more cold surface area that tends to quench combustion reactions and produce higher levels of unburned carbon than the pilot-scale unit used in EPA's combustion tests of Orimulsion. Figure 9-7 shows the particle size distributions measured by an Andersen impactor for the No. 6 fuel oil and the emulsified No. 6 fuel oil tested in the firetube boiler in the 1995 tests. Over 70% of the particle mass from the emulsified No. 6 fuel oil are smaller than 2.5 µm in diameter, compared to less than 40% of the particle mass from the non-emulsified No. 6 fuel oil.

These results can be directly compared to those presented earlier in Figure 5-7. The No. 6 fuel oil tested during the Orimulsion pilot-scale tests showed approximately 45% of particle mass smaller than 0.3 µm in diameter, compared to only 6% of particle mass smaller than 0.4 µm in the 1995 tests conducted in the firetube boiler. This is most likely due to the higher level of unburned carbon in the firetube boiler samples compared to the pilot-scale combustor used in the Orimulsion tests (Miller et al. 1998a). Even with the greater percentage of larger particles, the emulsification of the No. 6 fuel oil results in a significant shift of the particle size distribution toward smaller particles. Figure 9-7 shows that the emulsified No. 6 fuel oil has over 25% of particle mass in particles smaller than 0.4 µm in diameter. Using the emulsified No. 6 fuel oil clearly results in smaller particle sizes. This shift is also seen when comparing the No. 6 fuel oil used in the Orimulsion pilot-scale tests with the particle size distributions from both Orimulsion formulations, although not to the same degree as seen in the 1995 tests.

Hazardous Air Pollutants Emissions and Control
HAPs from the combustion of fossil fuels are generally low as measured by stack gas concentration, and, with a few exceptions, low in terms of total mass emissions. The threshold level of regulatory concern for HAPs is 10 tons/year of any single HAP and 25 tons/year of any combination of HAPs from a single source. For utility boilers firing coal, only HCl and HF are found to be above these annual mass emission levels with any significant frequency. The other HAPs of concern in utility emissions, such as mercury, are of concern because of the total mass emissions of the industry rather than of a single source. Mercury is of most concern because of its persistence in the environment and its bioaccumulative behavior. Organic HAPs are typically found in very low trace concentrations, if at all, in utility stack gases. The Utility Study did not find the health risks from organic HAPs, including dioxins and furans, to be significantly increased due to utility emissions (EPA 1998).

Organic emissions from Orimulsion have been measured as being of roughly the same level as those from coal and heavy fuel oil combustion. In general, organic HAPs from the combustion of Orimulsion are very low, and the results to date indicate that such compounds are not likely to be emitted at significantly higher levels than are found in coal and heavy fuel oil stack gases. Because
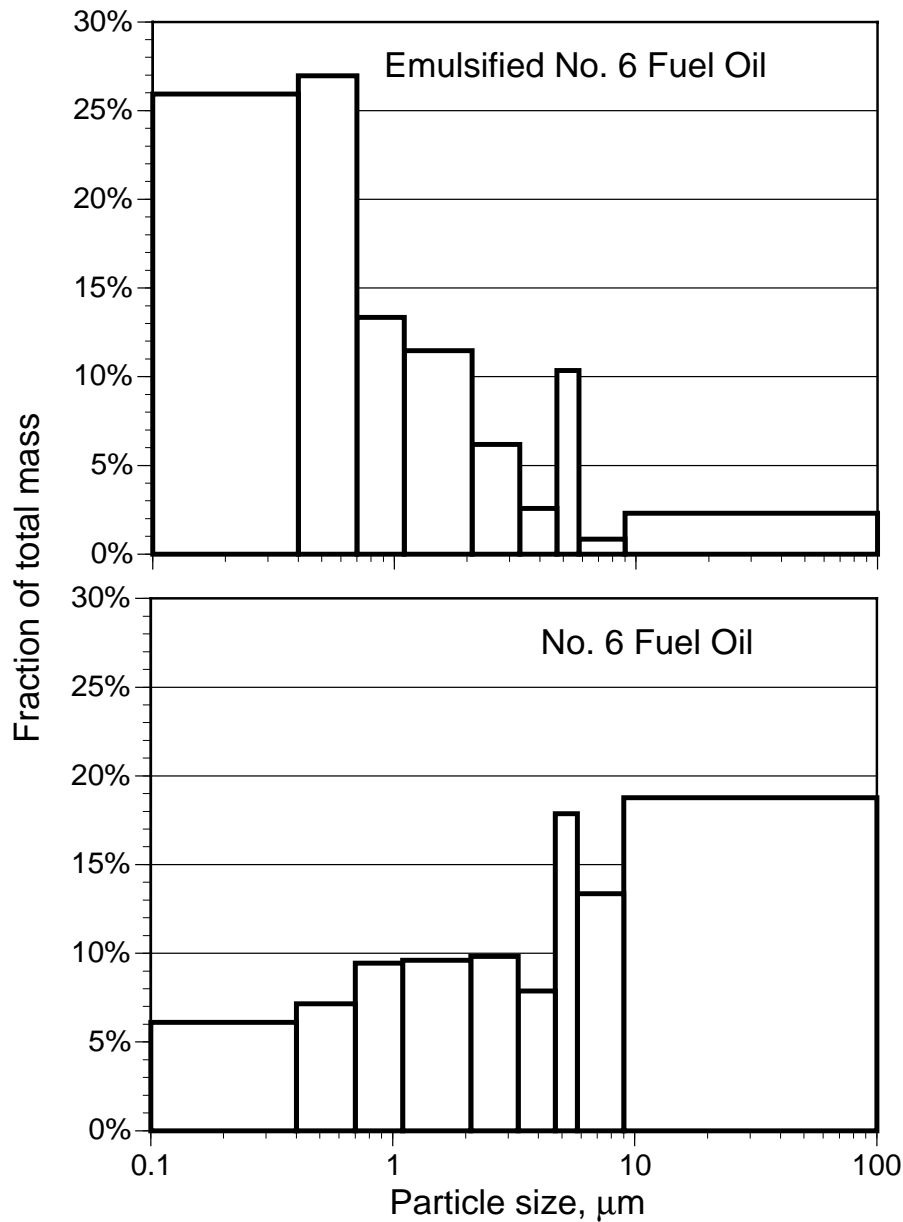
Figure 9-7. Particle size distributions for a No. 6 fuel oil and the same fuel oil in a 90% oil/10% water emulsion.

of the very low concentrations and the low annual mass emissions, there have not been any demonstrations of organics controls implemented for utility boilers, and such controls have not been proposed. The conventional view of controlling organics emissions is to maintain adequate combustion O_2 and adequate temperature, which are also operating practices that are desirable for optimum efficiency and are routinely followed.

Metal HAPs are strongly influenced by the concentration of the metals in the fuel. As noted earlier in this section, coal typically contains arsenic, chromium, mercury, and nickel. Heavy fuel oil often contains significant levels of nickel. Natural gas is normally considered to have few impurities, although trace levels of sulfur are usually present. Nickel is the only metal found in Orimulsion in

significant quantities that is also listed as a HAP under Title III of the 1990 CAAAs (Clean Air Act 1990). The levels of Ni found in Orimulsion are similar to those in heavy fuel oil, on the order of 50 ppm. Ni is controlled primarily through control of solid particles, using an ESP or fabric filter. As noted above, conventional PM control equipment can be used on an Orimulsion-fired unit, if adequate allowance is made for the higher flue gas volumetric flow and the potential corrosion due to SO_3 condensation.

Pulverized coal tends to have higher levels of metals listed as HAPs under Title III, and the plants burning coal are on average larger than oil-fired plants, resulting in higher total emissions of metal HAPs. The 1996 study of HAP emissions from utility boilers indicated that the metal having the most potential for concern was mercury (EPA 1998). Coal-fired utility boilers account for a substantial percentage of anthropogenic mercury emissions into the atmosphere (EPA 1998). However, Orimulsion does not contain measurable amounts of Hg, and is not expected to be a significant source of Hg emissions.

Transition Metals Emissions and Control
Transition metals are those metals that lie between groups 2 and 13 on the periodic chart. Of most concern relative to fossil fuel combustion are Cu, Fe, Ni, Zn, and V, due to their abundance in fossil fuels. Of these metals, only Ni is also listed as a HAP. Fossil fuels may also contain cobalt (Co), Cr, Mn, or Cd. The primary reason for concern regarding emissions of transition metals is their potential role in causing acute pulmonary damage upon inhalation (Dreher et al. 1996a, 1996b, 1997).

Orimulsion contains high levels of Ni and V compared to many other fossil fuels, although there are residual fuel oils that are also high in these elements (see Table 9-3). In addition, refined fuel oils may contain Zn introduced during the refining process. This was seen in the higher Zn level of the No. 6 fuel oil used in the EPA pilot-scale tests discussed in Chapter 5. Coals tend to have higher levels of Cu, Fe, and Zn than Orimulsion or residual fuel oils, but the total amount of coal burned in the U.S. is much higher than that of fuel oil, resulting in higher total mass emissions of these compounds compared to those originating from residual fuel oil use.

As was the case for metal HAPs, control of transition metals is most often achieved by conventional PM control equipment such as ESPs or fabric filters. Proper design and operation is required for these systems to be used in Orimulsion applications, but the full-scale results reported in Chapter 3 indicate that these systems can be successfully used to control transition metals from Orimulsion combustion.

CO_2 Emissions
CO_2 emissions are not currently regulated in the U.S., but are of considerable interest due to the role CO_2 is suspected to play in global climate change. CO_2 is produced by the combination of fuel-bound carbon and atmospheric O_2, and is dependent upon the amount of carbon per unit energy in the fuel. Of the three major fossil fuels (coal, fuel oil, and natural gas), coal has the highest amount of carbon per unit energy, followed by fuel oil and natural gas. Natural gas is primarily methane, CH_4, and therefore has significantly lower CO_2 emissions than either fuel oil or coal, which have much higher ratios of carbon to hydrogen. On a molar basis, natural gas has a carbon to hydrogen ratio of roughly 1 to 4, which translates to a mass ratio of roughly 3 to 1 due to carbon's higher molecular weight. Coal, on the other hand, has carbon to hydrogen mass ratios near 15 to 1 and will release between 60 and 75 lbs carbon per 10^6 Btu (Keppeler 1998). Fuel oil has carbon to hydrogen mass ratios ranging roughly between 6 and 9 to 1, with carbon release rates near 47 lbs carbon per 10^6 Btu (Reed 1998a). Orimulsion falls into the range of the fuel oils, with a carbon to hydrogen mass ratio of roughly 8 to 1 and a carbon release rate of about 46 lbs carbon per 10^6 Btu (see Table 5-1).

Thus, Orimulsion will generate less CO_2 per unit energy input (and per unit production) than will coal. This advantage of Orimulsion over coal is being exploited in Denmark, where the conversion from coal to Orimulsion at the Asnaes Power Station is credited with reducing CO_2 emissions by 16%.

This reduction is 5% of Denmark's total national target reduction of 20% (Miller and Shores 1999). Orimulsion will generate roughly the same CO_2 per unit energy as fuel oil, and more than natural gas.

Summary of Air Pollutant Emissions

The preceding sections have pointed out the fact that air pollutants are generated by all fossil fuels. Orimulsion must be evaluated in comparison to these other fuels and not in isolation. The issues of concern with regard to Orimulsion are also of concern with respect to heavy fuel oil and coal in particular. Developing issues such as $PM_{2.5}$ require that several characteristics of pollutant formation and emission be considered as possibly resulting in adverse environmental impacts, regardless of the fuel being used. While formation and emission of submicron particles, SO_2, and transition metals are of concern with respect to Orimulsion, these characteristics are also of concern with respect to other fuels.

Chapter 10
Quality Assurance

Quality assurance (QA) is the process of documenting the steps taken to ensure that measured data are adequate to support the conclusions drawn from them. Measurements of data uncertainty, variability, and error can provide an understanding of how closely a reported measurement represents the actual variable of interest.

Data Reported in Literature

Most of the reports in the literature do not address QA issues. CEM calibration, measurements of variability (such as maximum, minimum, and standard deviation) are often not reported, even if they have been measured. For this reason, one must evaluate the reliability of such data through other means. In the case of Orimulsion, several reports documented QA measures to some degree. These reports were the Carnot, Inc. report on emissions testing at the Dalhousie plant in Canada (Janati 1997), the Entropy report on the Orimulsion trials at the Sanford Plant in Florida (Entropy 1991), and the SK Power report on emissions testing at the Asnæs Power Station in Denmark (SK Power undated). In each case, the reports provided substantial background on the measurements taken. The background information included discussion of sampling methods, identification of any problems during sampling, and reporting of all results, including average and standard deviations.

In addition to these reports, several site visits were made by EPA to plants operating with Orimulsion to observe operation and gather information. During the visit to the Asnaes plant, discussions were held with plant personnel regarding steps taken to ensure CEM data quality. The staff at the Asnaes plant followed procedures that were similar to those used in the U.S. The Asnaes QA procedures will be discussed following a discussion of in-house QA activities.

In-House Combustion Testing

The testing described in Chapters 4 and 5 was conducted under an approved APPCD Level II Quality Assurance Project Plan (QAPP) titled *QAPP for Characterization of Orimulsion Emissions* dated March 1999 and the Addendum dated April 9, 1999. The plan set forth the operating, sampling, and analysis procedures to be used during the testing, as well as the data quality indicator (DQI) goals for the project.

Data Quality Indicator Goals

The DQI goals established in the QAPP for all critical measurements are shown in Table 10-1. The following sections summarize calculated DQIs in terms of accuracy, precision, and completeness.

Sampling critical measurements included continuous emission monitor measurements and combustor parameters such as temperature, pressure, and air flows. Table 10-2 is a summary of the CEM quality control (QC) checks. CEM calibration was verified by performing mid-point and span checks daily, before and after testing. The table shows average values taken from 17 days' worth of testing. The percent bias is calculated using Eq. 10-1 from the average of pre- and post-test checks.

$$Percent\ bias = \frac{measured\ concentration - known\ concentration}{known\ concentration} \times 100\% \qquad 10\text{-}1$$

Precision is expressed as percent relative standard deviation (RSD) and is calculated from

$$SD = \frac{standard\ deviation\ of\ replicate\ measurements}{average\ of\ replicate\ measurements} \times 100\% \qquad 10\text{-}2$$

by determining the standard deviation between the pre- and post- test values of the 34 replicates.

Completeness is expressed as a percentage of the number of valid measurements (i.e., meeting their

specified DQI goal) compared to the total number of measurements taken, and is given by:

$$Completeness = \frac{amount\ of\ valid\ data\ collected}{total\ amount\ of\ data\ collected} \times 100\% \qquad 10\text{-}3$$

Numbers shown in italic print in Table 10-2 did not meet the DQI goals established in the QAPP.

System bias checks were not done until after an internal technical systems audit was performed by EPA's on-site contractor on May 25, 1999. Immediately following the internal audit, system bias checks were performed with an available gas standard. Additional system bias checks were performed at the start of each test day. Results are tabulated by date in Table 10-3. The DQI goal for system bias checks was ±5%. As can be seen in the table, the mid-level standard for a ppm level of CO did not pass. O_2 and NO_x values also fell slightly out of range on the system bias check conducted May 28, 1999 and the NO_x value also failed on the system bias check conducted June 8, 1999.

Table 10-1. Data quality indicator goals for critical measurements.

Parameter	Method	Accuracy (% Bias)	Precision (% Difference)	Completeness (%)
Particulate Weights	Gravimetric	±0.1 mg based on weight	<±0.5 mg agreement between successive weights	>70
Volume Sampled	Dry Gas Meter	±5	±2	>70
Semivolatile organic compounds	Method 0010	±2	NA[1]	>90
	SW846 8270	10-140 % recovery	30%	
Volatile organic compounds	Method 0030	±2	NA	>90
	SW846 8260	50% recovery	30%	
CO	CEM	calibration ±2 drift ±3 system bias ±5	±7	>90
NO_x	CEM		±5	
O_2	CEM		±7	
SO_2	CEM		±5	
THC	CEM		±5	
Temperatures	Thermocouple	±2	±5	>90
Fuel Flow	Volume Totalizer	±10	±15	>90
Fuel Analysis	Ultimate and Proximate	±5	±5	>90
Pressure	Manometer	±10	±10	>90
Fuel Lower Heating Value	ASTM[2] D240	Not Available	0.5 kJ/kg	>90
TCLP	SW846	±10	±10	>90
Loss on Ignition	Thermogravimetric	±10	±5	>90

1. Not applicable
2. American Society for Testing and Materials

Calculation of DQI Values

The quality controls checks in place to determine whether or not DQI goals were met for sampling and analytical activities are summarized in the following sections. Results of specific DQI goals in terms of accuracy, precision, and completeness are tabulated.

Sampling Goals

Assessment of CEM DQI goals for span checks is summarized in Table 10-2. Accuracy for CEM measurements is expressed as percent bias and was calculated using the averaged value of replicate measurements. Precision, in terms of percent relative standard deviation (RSD), was calculated for replicate analyses. Values that did not fall within DQI goals are in italic text.

System bias checks were performed by running known concentrations of span gases through the entire system and measuring concentrations using the same methods used to measure sample gas concentrations. Table 10-3 summarizes the results of the system bias checks that were performed between May 25 and June 7, 1999. Checks that did not meet DQI goals are indicated by italic text.

Analytical Data Quality Indicators

Samples were submitted for analysis of volatile and semivolatile organic compounds. Criteria were established for recovery, precision, and completeness. Assessment of DQI goals is discussed in the following subsections.

Volatile Organic Compounds

VOCs were analyzed using Method 5041. Calibrations ranged between 10 ng and 250 ng on each column. Internal standards were injected into the sidearm of the sparging vessel during each calibration and analysis. All target analytes had a relative standard deviation less than 30% for this initial calibration.

A 6-point method detection limit (MDL) study was done by the Organic Support Laboratory prior to

Table 10-2. CEM full-range and mid-range span check results. Values in italics did not meet DQI goals.

CEM	Span range	Actual	Measured (average)	% Bias	Precision (%RSD)	Completeness (%)
CO (ppm)	Full	850	855	0.6	3.9	92
	Mid	309	347	*10.1*	5.4	*12.5*
CO_2 (%)	Full	15.1	14.9	1.3	4.3	*85*
	Mid	7.98	7.23	*9.4*	2.3	*3*
NO_x (ppm)	Full	762	771	1.2	4.6	76
	Mid	210	216	2.6	6.5	53
O_2 (%)	Full	14.8	14.88	0.5	2.3	94
	Mid	8.06	8.12	0.7	2.7	91
THC (ppm)	Full	92	89	3.3	*6.5*	*68*
	Mid	11	8.4	1.3	*36.2*	*24*
SO_2 (ppm)	Full	2190	2180	0.5	2.3	100
	Full	4,000	3865	3.4	*7*	*78*
	Mid	1,010	1021	1.1	*6.7*	*44*

analyzing project samples by spiking and analyzing a clean VOST pair spiked with 10 ng of each target VOC and surrogate VOC in accordance with SW-846 methodology for determining MDLs. The target list of analytes along with the established MDLs for each analyte are shown in Table 10-4.

A mid-level standard was analyzed daily prior to sample analysis. Relative percent deviations less than 30% when compared to the average response factors calculated using the initial calibration were found for all target analytes of interest.

Sample VOST tubes were spiked prior to field sampling with surrogate compounds specified by the method. Surrogate recoveries are summarized in Table 10-5. Samples that did not meet established recovery criteria are shown in italic text.

Replicated matrix spikes of a separate benzene, toluene, ethyl benzene, and xylenes (BTEX) standard were performed using flash evaporation. Matrix spike and matrix spike duplicate (MS/MSD) results are summarized in Table 10-6. All recoveries and percent difference values fell within the established acceptable limits.

The VOC field blank demonstrated that all compounds were below the calculated detection limits except for dichloromethane, which fell directly on the detection limit of 3.7 ng.

Semivolatile Organic Compounds

Semivolatile organic compound (SVOC) analysis was performed according to Method 8270. A rigorous method detection limit study was not performed prior to sample analysis. Past SVOC analysis allowed insight for establishing an arbitrary 1 ug/mL for the instrumental detection limit. Sample concentrations near this value were scrutinized carefully to ensure retention time matching and adequate confirmation ion ratios.

Table 10-3. CEM system bias check results. Values in italics did not meet DQI goals.

	Full-range Bias Check			Mid-range Bias Check		
	Actual	Measured	% Bias	Actual	Measured	% Bias
5/25/99 bias check results						
O_2 (%)	14.8	14.98	1.2	8.06	8.45	4.8
CO_2 (%)	15.1	15.6	3.3	7.98	7.7	3.6
CO (ppm)	850	841	1.1	309	361	*16.8*
5/28/99 bias check results						
NO_x (ppm)	762	708	*7.1*	210	207	1.4
O_2 (%)	14.8	15.43	4.3	8.06	8.77	*8.8*
6/3/99 bias check results						
O_2 (%)	8.06	8.16	1.2	NC[1]	NC	NC
6/7/99 bias check results						
O_2 (%)	15.2	15.6	2.6	NC	NC	NC
CO_2 (%)	15.2	14.9	2	NC	NC	NC
NO_x (ppm)	762	635	*16.7*	NC	NC	NC

1. Not conducted.

10-4

Daily QC measures included an initial passing of the decafluorotriphenylphosphine (DFTPP) tuning criteria. The presence of benzidine in the DFTPP tuning solution was tested and the monitoring of dichlorodiphenyltrichloroethane (DDT) for lack of degradation was done daily prior to sample analysis. After the DFTPP tune phase, a mid-point calibration standard was analyzed. The mid-level standard was compared to the response factors obtained during the initial calibration curve. Relative standard deviations of all constituents of interest were less than 30%.

Three samples were run outside the method specified limit of 12 hours from the time of running a standard. The samples in question were the XAD and filter portions of the field blank and the XAD extract from the June 3, 1999, No. 6 fuel oil run. There does not appear to be any adverse effect on data quality due to this oversight.

The 40 day hold time from extraction to analysis was exceeded by 4 days for the first set of No. 6 fuel oil samples. The runs at these conditions were repeated and the initial samples were not used.

Table 10-7 summarizes the results from the analysis of the matrix spike/matrix spike duplicate in terms of recovery and percent difference and completeness. All values were within the established DQI goals with the exception of di-n-butylphthalate, which had a recovery of only 10%.

Table 10-4. VOC target analytes and method detection limits.

Analyte	MDL (ng)	Analyte	MDL (ng)
1,1-Dichloroethene	1.6	Bromodichloromethane	3.3
Iodomethane	3.5	c-1,3-Dichloropropene	3.5
Carbon disulfide	1.7	Toluene	2.3
Dichloromethane	3.7	t-1,3-Dichloropropene	4.4
t-1,2-Dichloroethene	1.3	1,1,2-Trichloroethane	4.5
1,1-Dichloroethane	1.6	Tetrachloroethene	5.2
c-1,2-Dichloroethene	1.5	Dibromochloromethane	6.1
Bromochloromethane	2.6	1,2-Dibromoethane	6.2
Chloroform	1.7	Chlorobenzene	4
1,1,1-Trichloroethane	1.2	Ethylbenzene	3.7
Carbon Tetrachloride	1.1	m,p-Xylenes	7.1
1,2-Dichloroethane	2.4	o-Xylene	4.5
Benzene	2.9	Styrene	4.6
Trichloroethene	3.3	Bromobenzene	4.4
1,2-Dichloropropane	3.7	1,4-Dichlorobenzene	4.2
Dibromomethane	3.4	1,3-Dichlorobenzene	4.3
		1,2-Dichlorobenzene	4

Table 10-5. VOC surrogate recovery results. Values in italics did not meet DQI goals for recovery.

Sample ID	d4[1] 1,2-Dichloroethane	d8[1] Toluene	4-Bromofluorobenzene
905031354	94.2	92.2	93.6
905041257	94.1	102.1	79.8
904301255	92.9	98.4	117.1
905181405	86.1	100.4	119.7
905194058	84.1	97.3	107.6
905211256	85.5	*32.2*	109.1
905441337	65.8	94.1	115
905251243	100.9	71	119.8
905261102	73.1	96.3	117
906031301	*64.7*	90.7	123.9
906011340	*57.3*	95.5	*134.1*
906071305	*64.5*	82	*157*
90430123/FB[2]	91.6	101.6	120.6
MS	86.6	103.9	112.7
MSD	87.5	89.4	112.5
Average	81.9	89.8	116
Completeness	11/15=73.3%	14/15=93.3%	13/15=86.7%

1. Deuterated compound
2. Field blank.

Table 10-6. VOC matrix spike and matrix spike duplicate results.

Compound	Spiked (µg)	MS (µg)	% Recovery	MSD (µg)	% Recovery	% Difference
Benzene	150	135	90	130.4	86.9	3.5
Toluene	150	145.3	96.9	139.9	93.3	3.8
Ethylbenzene	150	161.4	107.6	169	112.7	4.6
m,p-Xylene	150	173.8	115.9	172	114.7	1
o-Xylene	150	168.8	112.5	172.9	115.3	2.4

Table 10-7. SVOC matrix spike and matrix spike duplicate results. Values in italics did not meet DQI goals for recovery or percent difference.

Compound	Spiked (ug)	Matrix spike recovery (%)	Matrix spike duplicate recovery (%)	Average Recovery (%)	Percent difference
Naphthalene	100	55	50	52.5	9.5
Acenaphthylene	100	62	53	57.5	15.7
Acenaphthene (CCC)	100	59	52	55.5	12.6
Fluorene	100	69	61	65	12.3
Phenanthrene	100	72	66	69	8.7
Anthracene	100	73	67	70	8.6
Di-n-butylphthalate	100	*10*	*5*	*7.5*	*66.7*
Fluoranthene (CCC)	100	75	71	73	5.5
Pyrene	100	75	69	72	8.3
Benzo(a)anthracene	100	75	69	72	8.3
Chrysene	100	75	69	72	8.3
Benzo(b)fluoranthene	100	72	67	69.5	7.2
Benzo(k)fluoranthene	100	76	72	74	5.4
Benzo(a)pyrene	100	77	72	74.5	6.7
Indeno(1,2,3-cd)pyrene	100	73	67	70	8.6
Dibenzo(a,h)anthracene	100	73	67	70	8.6
Benzo(g,h,9)perylene	100	73	67	70	8.6
Completeness	16 of 17 compounds met DQI goals for recovery and percent difference, for completeness of 94%				

Table 10-8 summarizes recovery values of pre-extraction surrogates. The following compounds were added to each sample prior to extraction:

- 2-fluorophenol (surrogate 1E)
- d5-phenol (surrogate 2E)
- 2,4,6-tribenzophenol (surrogate 3E)
- d5-nitrobenzene (surrogate 4E)
- 2-fluorobiphenol (surrogate 5E)
- d14-terphenyl (surrogate 6E)

Filter samples are indicated with an "F" in the sample ID, XAD samples are followed by an "X," and condensate samples are followed by a "C." Acceptable recovery limits varied slightly for each compound but ranged from 19 to 135%. Compounds that did not meet DQI goals for recovery are shown in italic text. Out of a total of 39 samples, only 3 samples did not meet DQI goals for one or more compounds.

Table 10-9 summarizes pre-sampling surrogate recovery values. Pre-sampling surrogates were only

Table 10-8. SVOC pre-extraction surrogate recovery levels.

Sample ID	Surrogate 1E	Surrogate 2E	Surrogate 3E	Surrogate 4E	Surrogate 5E	Surrogate 6E
904301209F [1]	46	54	77	51	53	100
904301209X [2]	42	48	75	53	63	91
904301209C [3]	34	32	60	46	49	83
905041052C	43	40	73	59	57	98
905031315C	30	29	50	39	39	72
905031315X	67	56	95	83	87	115
905051149C	50	47	72	62	61	101
905031315F	56	51	95	75	78	108
905041052F	55	52	75	69	70	82
905041052X	48	46	72	56	61	89
905051149F	35	44	56	41	47	69
905051149X	41	48	51	45	46	74
905181131F	59	71	87	70	72	93
905181131X	80	66	101	89	92	128
905191016F	51	61	78	58	62	105
905191016C	39	34	87	64	67	113
905191016X	60	61	89	68	72	119
905211135F	44	53	80	52	57	101
905211135X	56	57	84	63	67	115
905211135C	34	25	79	59	55	112
905241202F	51	60	78	59	62	106
905241202X	54	59	78	63	64	98
905241202C	36	31	78	56	55	118
905251144F	50	62	75	59	61	106
905251144X	55	60	90	61	65	114
905251144C	39	35	77	61	59	127
905261054F	49	62	83	56	62	117
905261054X	41	53	94	56	67	120

(continued)

Table 10-8. SVOC pre-extraction surrogate recovery levels (continued).

Sample ID	Surrogate 1E	Surrogate 2E	Surrogate 3E	Surrogate 4E	Surrogate 5E	Surrogate 6E
905261054C	42	34	77	62	60	108
906031216F	42	56	85	56	68	116
906031216X	48	58	85	60	66	108
906031216C	30	25	57	45	42	83
906041304F	42	57	75	59	65	105
906041304X	48	62	91	65	71	123
906041304C	51	46	98	74	74	131
906071229C	58	50	105	80	80	-138
906071229F	56	68	95	73	75	118
606071229X	72	85	*-144*	87	91	*-144*
Resin Blank	67	83	113	82	85	*-154*
Complete-ness	36 samples out of 39 met DQI goals for recovery = 92%					

1. "F" denotes filter.
2. "X" denotes XAD.
3. "C" denotes condensate.

spiked on XAD samples and contained the following compounds:

- 13C6 1,2-dichlorobenzene (Surrogate 1S)
- 13C6 naphthalene (Surrogate 2S)
- D10-anthracene (Surrogate 3S)
- 13C6 2,5-DCP (Surrogate 4S)
- 13C6 2,5-PA (Surrogate 5S)

Pre-sampling surrogates were considered experimental and no acceptance criteria for recovery were established. However, in general, recoveries were qualitatively very good.

Metals Analyses
Metals were analyzed by Prism Laboratories, Inc. using EPA Method 29, Determination of Metals Emissions from Stationary Sources. Laboratory data sheets are included in Appendix E. A report was received from Prism Laboratories that contained analytical results, chain-of-custody records, and QA/QC data. Table 10-10 is a tabulated summary of the internal matrix spike analysis to assess method accuracy, and duplicate sample analysis for precision assessment. The acceptance criterion for recoveries established by the method as passing is 75-125%. Values shown in italics did not pass recovery acceptance criteria. The acceptance criterion established for percent relative standard deviation (RSD) between duplicates was 20%. All duplicate analyses passed this criterion.

Table 10-11 shows recovery results from two spiked samples sent to the laboratory. A mixture containing 100 μg of each target metal (metals listed in Table 10-11) was spiked onto clean filters and submitted to the laboratory for analysis. These data could be considered an internal performance evaluation audit. Recoveries for all spiked materials fell within acceptable DQI goals for recovery of 75-125%.

Laboratory blanks were generally below detection limits. A reported value for arsenic of 30.6 μg exceeded blank acceptance limits for samples analyzed on July 12, 1999. This will be taken into

consideration when evaluating arsenic sample data analyzed with the same batch.

Audits
This project was performed under a QA Category II assignment. A Category II assignment requires that internal and EPA audits be performed during the project. An internal systems audit was performed by the EPA on-site contractor QA Officer on May 25-26, 1999. A checklist was prepared by the EPA on-site contractor QA Officer using the *QAPP for Characterization of Orimulsion Emissions* (dated March 1999) and the Addendum to the QAPP (dated April 9, 1999). Calibration, start-up, and sampling (CEMs, VOCs, SVOCs, and particulate) activities were observed. Project documentation was also reviewed for completeness and adequacy. An internal audit report detailing findings and observations was submitted to the EPA on-site contractor work assignment leader on June 2, 1999.

In addition to the internal audit, a performance evaluation and technical systems audit were also performed by the EPA QA Representative.

Audit Summary
It was noted in both the internal and EPA audits that project documentation by the staff of EPA's on-site contractor (ARCADIS Geraghty & Miller, hereafter referred to as ARCADIS) could be improved. Several changes to the fuel feed system and modifications to CEMs that were made during the course of the project had not been adequately documented in the project notebook. Findings from both audits noted that CEM quality control checks as specified in the QAPP were not being performed. Sampling and operation personnel demonstrated that they were familiar with methods used to perform their assigned task and it was evident that personnel were familiar with the approved QAPP, even though there were some deviations from the document. It was noted that, at the time of the audit, deviations had not been formally documented by project personnel.

Table 10-9. Pre-sampling surrogate recovery/XAD samples.

Sample ID	Surrogate 1S	Surrogate 2S	Surrogate 3S	Surrogate 4S	Surrogate 5S
904301209X	48	57	76	65	96
905031315X	83	88	98	89	161
905041052X	54	57	73	61	126
905051149X	46	46	61	45	9
905181131X	86	87	100	92	142
905191016X	66	67	86	70	70
905211135X	66	67	82	68	57
905241202X	64	66	72	71	116
905251144X	61	64	86	64	97
905261054X	46	55	75	61	218
906031216X	49	54	73	58	165
906041304X	53	61	73	63	45
906071229X	59	63	78	64	29

Table 10-10. Internal laboratory QC summary.

Metal	Fraction	Accuracy			Precision		
		Spiked (µg)	Measured (µg)	Recov- ery (%)	1st Analysis	Duplicate Analysis	RSD (%)
Antimony	0.0416667	384	294	77	<2	<2	0
	0.0416667	384	350	91	32	32	0
	0.0833333	288	231	80	<1.5	<1.5	0
	0.0833333	288	252	88	<1.5	<1.5	0
Arsenic	0.0416667	384	314	82	10	8.5	16
	0.0416667	384	338	88	9.3	8.6	7.8
	0.0833333	288	348	121	1.5	1.5	0
	0.0833333	288	278	97	<1.5	<1.5	0
Beryllium	0.0416667	384	316	82	23	23	0
	0.0416667	384	347	90	20	20	0
	0.0833333	288	259	90	<1.5	<1.5	0
	0.0833333	288	243	84	1.8	1.8	0
Cadmium	0.0416667	384	307	80	6.8	6.8	0
	0.0416667	384	335	87	9	8.5	5.7
	0.0833333	288	225	78	1.5	1.5	0
	0.0833333	288	249	86	3	3	0
Chromium	0.0416667	384	332	86	8.2	8.2	0
	0.0416667	384	358	93	30	30	0
	0.0833333	288	246	85	2.4	2.4	0
	0.0833333	288	264	92	1.6	1.6	0
Copper	0.0416667	384	360	94	17	16	6
	0.0416667	384	381	99	70	70	0
	0.0833333	288	249	86	4.8	4.9	2.1
	0.0833333	288	261	91	3	2.9	3.4
Iron	0.0416667	3840	3150	82	69	70	1.4
	0.0416667	3840	3100	81	69	68	1.5
	0.0833333	2880	2400	83	101	102	1
	0.0833333	2880	2415	84	30	30	0

(continued)

10-11

Table 10-10. Internal laboratory QC summary (continued).

Metal	Fraction	Accuracy			Precision		
		Spiked (μg)	Measured (μg)	Recov-ery (%)	1st Analysis	Duplicate Analysis	RSD (%)
Magnesium	0.0416667	3840	3010	78	1510	1508	1.3
	0.0416667	3840	3390	88	69	70	1.4
	0.0833333	2880	2130	*-74*	3045	3060	0.5
	0.0833333	2880	2340	81	<15	<15	0
Manganese	0.0416667	384	320	83	19	19	0
	0.0416667	384	351	91	42	43	2.3
	0.0833333	288	236	82	2.2	2.3	4.4
	0.0833333	288	248	86	<1.5	<1.5	0
Nickel	0.0833333	288	213	*-74*	695	700	0.7
	0.0833333	288	256	89	<1.5	1.6	6.4
Vanadium	0.0833333	288	120	*-43*	3420	3435	0.4
	0.0833333	288	260	90	21	21	0
Zinc	0.0416667	384	238	-62	<2	<2	0
	0.0833333	288	236	82	11	12	8.6
	0.0833333	288	243	84	9.7	9.6	1
Completeness		39 samples pass/43 total samples = 90.7%					

Findings and Observations

Findings were reported by both the EPA QA Representative and the ARCADIS QA Officer as a result of their respective audits. Specific findings and observations are listed in the following sections. These items are discussed in detail in the respective audit reports that were submitted by QA to the EPA and ARCADIS project managers.

EPA Performance Evaluation and Systems Audits

A performance evaluation audit (PEA) of several project measurements was conducted by EPA QA staff from NRMRL's Technical Services Branch. The PEA report focused on three findings: flue gas flow, fuel feed rate, and CEMs. Comments by EPA's QA auditor are summarized below for each finding.

Flue Gas Flow

For ducts smaller than 0.3 m (12 in.), EPA Method 1A should be used to determine stack flue gas flow rates. In Method 1A, a standard pitot tube is specified, but in these tests, an "S"-type pitot tube was used.

To determine flue gas flow rates, velocity measurements are taken at specified locations across the duct (traverse points). The traverse locations listed in the data sheet for June 7, 1999, were not correct, although the marks on the ruler used to determine probe location were correct. The reason for this difference was unclear, but was not believed to have altered the resulting measurements. This is primarily due to the fact that the flue gas exhibited a very "flat" velocity profile across the duct, and slight changes to the traverse points would not have changed the measurements in any substantial

way. Data used to determine sampling isokineticity were consistent with the actual measurements taken, and no adjustment of the isokineticity results was required.

Fuel Input Flow
Measurements of fuel feed rate changed from approximately 0.984 gpm to 1.05 gpm during the period of examination on June 7, 1999. This drift contributed to the fluctuations in O_2 level measured during testing on this date, and possibly during earlier tests.

CEM Calibrations
There were 12 test runs conducted during the test program. During each test run, four calibration measurements were made (not including the zero point) for each CEM. These four measurements were pre-test checks of mid- and high-span values and post-test checks at the same two points. Of the 48 measurements for each of the 5 gases (240 total measurements), 47.5% (114) did not meet DQI goals. Of the 114 measurements that did not meet DQI goals, 85 were mid-span measurements, 28 were post-test high-span measurements, and 1 was a pre-test high-span measurement. A discussion of the impact of these measurement problems is presented in the Data Limitations section below.

Other Discrepancies
Several other discrepancies between standard sampling methods and methods used during the test program were noted during the EPA audit. For Method 29, these included using 125 mL of solvent rather than 100 mL as called for by the method, recording weights instead of volumes when measuring impinger contents, and spiking solutions rather than filters for QA samples. For measurements taken using the dilution sampler, the QAPP called for a 4-hour sampling time, while in actuality the measurements were taken until the pressure drop across the filter became excessive (at approximately 2 hr of sampling time). For the VOST samples, 2 pairs of cartridges were used rather than 6 pairs as called for in the method, but 3 runs (each using 2 cartridge pairs) were conducted for each test condition.

Of these "other" discrepancies, the most serious was that the technique used to determine CEM system bias did not follow the proper procedure, by connecting the calibration gas directly to the

Table 10-11. Spiked metal sample recoveries.

Target	Recovery (%)	
	Sample ID #907010942	Sample ID #907010943
Antimony	93	94
Arsenic	97	91
Cadmium	95	99
Chromium	99	101
Copper	104	104
Iron	121	124
Magnesium	99	100
Manganese	90	95
Nickel	93	95
Vanadium	96	98
Zinc	90	92
	Completeness 100%	

sample line rather than extracting the calibration sample at the same sampling pressure as the stack flue gases. This change may have impacted the ability of the bias check to identify leaks into the sample line.

ARCADIS Technical Systems Audit
The following specific findings and observations were included in the ARCADIS internal technical systems audit (TSA) report:

- Finding 1:   No CEM bias checks or independent calibration checks were performed on the CEMs.
- Finding 2:   Adequate leak checks around CEM system were not performed prior to testing.
- Observation 1: All required QC samples had not yet been prepared and submitted as of the date of the TSA (May 25 and 26, 1999).
- Observation 2: There was no indication/documentation that the balance used to weigh filters had been calibrated.
- Observation 3: Sample labels were not prepared with permanent ink.
- Observation 4: PBS operation notebook was not being routinely signed and dated by operator.
- Observation 5: There were minor deviations from the standard recovery methods. Example deviations include:
  - amber or tinted jars were not used
  - filter dishes were not sealed with Teflon tape
  - impinger weights were recorded instead of volume
  - 100 mL rinse solution was not used, rather jars were filled to a known mark after rinsing

The auditor did not feel sample integrity had been compromised by these deviations.

As a result of audit findings, a series of system bias checks were performed immediately following the ARCADIS internal systems audit and then done on at least a weekly basis until testing was completed.

Other Discrepancies
Several other problems that arose during testing are not believed to have adversely impacted data quality, but should be documented in this section. There were two main problems that required modification of procedures and test configurations. The first is the fuel system design, which was discussed briefly in Chapter 4. Initial short-term operation of the PBS with Orimulsion 400 indicated that no modification of the fuel system (shown in Figure 4-2) would be required to conduct testing of Orimulsion 100 or 400. However, during the first full day of testing with Orimulsion 400, the fuel system was found to have substantial amounts of "sludge" that did not flow reliably into the combustor. After discussing the situation with experts who had previously tested Orimulsion in pilot-scale facilities, the fuel feed system was redesigned to that shown in Figure 4-3. Following this modification, difficulties in maintaining O_2 levels were encountered, leading to installation of additional fuel regulators. The final design of the fuel feed system is that shown in Figure 4-3. The final configuration resulted in relatively steady operation, although the O_2 levels (and subsequently the CO levels) still tended to vary to a greater degree than desired.

The second problem encountered was that both Orimulsion 100 and Orimulsion 400 tended to settle to a slight degree in the drums. A gentle mixing was used to reduce the settling prior to feeding the fuel into the PBS, and subsequent operation did not indicate significant changes in fuel characteristics during testing.

Data Limitations
Of the discrepancies noted above, the most serious is the failure of the CEMs to meet the DQI goals for accuracy as measured by the calibration results. Of these, the majority (nearly 75%) were mid-span checks. The calibration procedure is to set the monitor zero point, followed by setting the high-

span point, then repeating the checks until the two are as close as possible to their respective setpoints. The mid-span calibration point will be met if the monitor has a linear relationship between actual and measured values at each point between the zero and the high-span calibration point. If, after the zero and high-span values have been set, the mid-span check does not agree with the calibration gas, then one concludes that the monitor is not linear between zero and the high-span value. Monitor linearity is important when the gas being measured is not near the zero or high-span points.

For these tests, mid-span checks showed the greatest deviation for CO and SO_2. For CO, the CEMs measured concentrations at the mid-span approximately 12-15% higher than the calibration gas concentration (309 ppm). The high-span calibration gas concentration was 850 ppm. Because the CO concentrations reported in Chapter 5 were below 100 ppm, the difference between actual and measured concentrations is likely to be lower than 12-15%. The reported CO concentrations are also likely to be slightly higher than the actual concentrations, but it is not possible to accurately estimate the difference other than by comparison to the mid-span differences. For SO_2, no mid-span calibrations were made, making it impossible to evaluate CEM linearity for SO_2. While nonlinear CEM performance may have contributed to the discrepancies between measurement methods and calculated concentrations (see Table 5-4), it is not believed that CEM nonlinearity was the major factor in the measurement differences.

In general, the discrepancies noted here are not believed to have a significant impact on the conclusions drawn from this study. This study is more concerned with measuring differences between the different fuels than with absolute concentrations. Since measurements for all three fuels were made using the same equipment, and since the measured deviations were consistent for all three fuels, the relative changes are believed to be primarily due to differences in fuels. As with any pilot-scale study, the absolute concentrations should be considered as indications of full-scale performance and not directly transferable to full scale.

QA Review of Sampling and Measurement Activities at Asnaes
NRMRL technical staff members conducted a site visit to the Asnaes Power Station in Kalundborg, Denmark to observe stack sampling activities and to gain an understanding of the procedures and methods used during the sampling. One of the major goals of this visit was to determine the degree of QA used by Asnaes during data collection and reduction, to allow an evaluation of the data quality for results published in several reports on Orimulsion pollutant emissions.

Flue Gas Concentration Measurements
Gas measurements made in Denmark follow international standards. International standards specify that all steps from sampling to recording and storage maintain performance characteristics to ensure that the measurement system is reliable and gives satisfactory results. Because this is in fact the same objective of the Environmental Protection Agency (EPA) methods, much of the sampling activities are similar, but not the same. ISO procedure number 7935:1992(E), titled "Stationary source emissions - Determination of the mass concentration of sulfur dioxide - Performance characteristics of automated measuring methods" was provided by the Asnaes Power Station personnel.

Three different organizations were responsible for data collection during the test campaign being conducted at Unit 5 during the site visit. The Asnaes power station personnel operate permanently mounted continuous emission monitors (CEM) at the inlet of the electrostatic precipitator (ESP) and at the stack. The Technical University of Denmark (DTU) operated particulate samplers and gaseous CEMs at the ESP inlet, outlet and at the stack. FLS Miljøs (a supplier of ESP and FGD equipment) operated particulate samplers at the ESP exit.

The Asnaes power station collected data for O_2, CO, CO_2, NO_x, SO_2, PM using CEMs, moisture, and stack gas and ambient temperatures. These data are collected continuously, not just for the short-term sampling effort. Instruments are calibrated using either compressed gases, certified by gas manufacturers using gravimetric standards, or by comparison to other measurement method techniques. Instrument response is evaluated on a daily to monthly basis, depending upon the scheduled operations. The instrument operations are evaluated every morning and corrective action

is taken as needed. The CEM data are collected every 10 seconds, averaged to 1/2 hour values and every 24-hour period are stored on a power plant computer. Spreadsheets are used to calculate monthly emissions rates and various other parameters reported by the plant. The spreadsheet has links to the 1/2 hour averages and a summary spreadsheet is stored for each month. The August 1999 summary was reviewed while discussing the formulas and values calculated for the month. Material collected includes calibration gas analysis certificates, data sheets used for QC activities and a printout of spreadsheet formulas. Documentation observed includes calibration log books and gas analysis certificates (kept in a locked cabinet) and various forms used for CEM operation. Calibrations, operations and data calculations are considered satisfactory to generate data that are representative of the process being evaluated and comparable to data collected in the United States.

PM Sampling Program

A PM sampling program was being conducted at Asnaes Unit 5 during the week of the site visit primarily to measure particle size distributions. Sampling points were at (1) the air preheater outlet upstream of the ESP; (2) the ESP outlet upstream of the FGD system; and (3) the FGD outlet (stack). The test program was designed by researchers at DTU to evaluate particle size distributions (PSDs) at different locations along the process. PSD measurements were being made using Berner cascade impactors and scanning mobility particle sizing (SMPS) systems at locations 1 and 2, and with impactors only in the stack.

DTU collected data for particle size distribution using eight stage impactors, sold by Hauge (located in Austria), and a scanning mobility particle sizer (SMPS) sold by TSI, and total particulate samples using in-stack filter holders. Impactor flow rate was provided using a German-made pump and regulated with a critical orifice, calibrated in the DTU laboratory. These samples were collected before the ESP, after the ESP and at the stack. The sampling location prior to the ESP contained too much particulate to operate the SMPS and a dilution probe was used to provide an appropriate concentration. The dilution probe also cooled the sample gas and lowered the dewpoint to parameter ranges acceptable to the SMPS. The dilution ratio was determined by continuously monitoring the carbon dioxide concentration of the raw gas within the duct and the concentration of the gas being analyzed. Because of the extended range of concentrations required for a 50:1 dilution ratio, two CEMs were operated.

The calibration gases used for calibration were certified by the specialty gas manufacturer using gravimetric standards. Because of low particulate concentrations, the sampling location after the ESP was not diluted. Cooling and moisture removal were conducted using permeable drying tubes, constructed of stainless steel. Sample gas flowed through a permeable SS tube surrounded by a drying agent. The stack gas flow rate and temperature were measured periodically using a standard pitot tube attached to an electronic manometer that calculated the stack gas velocity. These measurements were made 5 - 6 times a day. This frequency was considered acceptable because of the operating stability of the boiler and the stack gas concentrations. Impactor filters were collected using both aluminum and Teflon foils and various speciation analyses were conducted in the DTU laboratories.

Conversations with both the Asnaes personnel and the DTU researchers demonstrated a thorough understanding of sampling procedures and appropriate precautions to ensure acceptable data. Observed documentation included sampling forms, log books, and sample labels (impactor samples). The gaseous standards used for calibration had been certified by the specialty gas manufacturers using gravimetric standards. As described previously, the DTU sampling requirements are to adhere to ISO standards. Calibrations, operations and data calculations are considered satisfactory to generate data that are representative of the process being evaluated and comparable to data collected in the United States.

Personnel at Asnaes are in the process of formalizing their QA procedures in preparation for expected competition within the utility sector in Europe.

Toxicity Testing

Toxicity testing was conducted as a Category 2 project as defined in the 1996 NHEERL Quality Management Plan, and required preparation and approval of a Research Protocol that described the purpose, design, and analyses proposed for the testing (EPA 1999b). Reviews of the test plan and the results were required, as were several QC requirements during testing. The QC requirements were:

Maintenance of equipment service and audits;
Monitoring recovery of particles from filters;
Monitoring recovery of extracted particles;
Monitoring alterations to the physicochemical properties of extracted particles;
Using caged control animals to monitor pulmonary health status of animals;
Using saline-exposed animals to monitor effect of intratracheal instillation;
Providing duplicate exposure design for each dose employed; and
Including sentinel animals to monitor general health status of animals maintained in EPA facilities.

No discrepancies in the test procedures were noted.

Chapter 11
Conclusions and Recommendations

The purpose of this report was to respond to the request Congress made of EPA, "to provide better scientific data on the qualities and characteristics of this product and the potential environmental impact of its introduction" (U.S. House of Representatives 1997). It is not the objective of this report to address possible regulatory requirements or to estimate the costs associated with meeting such requirements. There are many site-specific factors that are determined by regulatory requirements that can significantly impact the cost of converting to Orimulsion. The data and the conclusions presented in this report should not be considered as endorsing or discouraging the use of Orimulsion, and the conclusions of this report cannot be considered as identifying specific approaches for meeting regulatory requirements. The conclusions presented here are technical and not regulatory in nature.

In response to the Congressional directive, NRMRL convened a panel of technical experts to evaluate EPA's proposed assessment plan. The peer review panel posed four questions at the beginning of the program (EPA 1999a). These questions are addressed below, based on the results of this study. After these specific questions have been addressed, further conclusions and recommendations are presented.

Responses to Questions of the Peer Panel

1. Are the emissions from the combustion of Orimulsion significantly different from those from other fossil fuels, and if so, how?

   <u>Emissions of air pollutants from Orimulsion are not fundamentally different from those from other fossil fuels</u>. From the perspective of air pollutant emissions, Orimulsion fundamentally behaves like a heavy fuel oil, and the air pollution control technologies applicable to heavy fuel oil are applicable to Orimulsion. The most significant difference in emissions characteristics is that PM emissions appear to be in a slightly smaller size range than those from heavy fuel oil, and are significantly smaller than those produced by pulverized coal combustion. Emissions of sulfur trioxide from Orimulsion also appear to be somewhat higher than for other fossil fuels, largely due to the high levels of sulfur and vanadium. Emissions of metals such as nickel and vanadium may also be higher than for other fossil fuels due to the higher level of these elements in the fuel.

   Pulmonary toxicity testing of captured PM from the two Orimulsion formulations and the No. 6 fuel oil used in the EPA in-house tests found PM derived from the combustion of Orimulsion 100 and Orimulsion 400 to be very similar to that from the No. 6 fuel oil in their ability to induce acute pulmonary toxicity.

2. Can the emissions from the combustion of Orimulsion be adequately controlled using existing air pollution control technologies? If not, are there modifications to existing technologies that can be made to adequately control emissions, or are new control technologies required?

   <u>Results from both full- and pilot-scale tests indicate that emissions from the combustion of Orimulsion can be adequately controlled using commercially available air pollution control technologies</u>. As with any application, proper design, operation, and maintenance are necessary to ensure adequate performance, but there is no indication that new technologies must be developed specifically for controlling air pollutant emissions from the combustion of Orimulsion or that major modifications to commercially available control technologies are required to adequately control emissions. However, significant modifications to fuel handling and storage systems, installation of air pollution controls, and/or modifications to boiler internal components may be required for successful conversion to Orimulsion from other fuels.

3. Is the behavior of Orimulsion during a spill significantly different than the behavior of other

fossil fuels, and if so, how?

The behavior of Orimulsion in a spill is significantly different than that of most other fossil fuels. The National Research Council (NRC) notes that emulsified fuels (of which Orimulsion is one) will behave very differently than non-emulsified fuels due to the presence of a surfactant. The surfactant will act to prevent coalescence of the particles into larger fuel particles or pools, making containment and recovery more difficult. Secondly, Orimulsion falls into the category of non-floating oils as defined by the NRC study. This characteristic of Orimulsion results in a likelihood of its sinking or remaining below the surface in a spill scenario, making it difficult (at best) to track any spill plume or recover the fuel, and which may increase its potential for contaminating public drinking water supplies. While tests have been conducted of Orimulsion spill containment and recovery systems in marine environments, there has been little work conducted on spills of Orimulsion in freshwater environments. While this issue should be addressed by Bitor as the need for such information arises, EPA should evaluate spill effects, behavior and response as appropriate in support of their legislated responsibility for spill prevention, preparedness, and response.

4. What gaps in understanding the behavior of Orimulsion exist, based on the behavior of other fossil fuels and the known properties of Orimulsion? Are these gaps serious with respect to understanding the potential environmental impacts, and if so, what research should be conducted to address these gaps?

The major gaps in understanding Orimulsion behavior are in the areas of health effects of inhaling fine particles and transition metals, and freshwater spill response and effects. There are indications that inhalation exposure to fine particles (particles smaller than 2.5 µm in diameter) and transition metals may contribute to adverse health effects. However, these problems are also present for other fossil fuels, and EPA is conducting numerous studies into the mechanisms associated with these health effects under their fine PM research program. Given the relatively low levels of Orimulsion that are likely to be used in the U.S. in the near term, the contribution of Orimulsion to ambient levels of fine PM is not likely to be significant on a national basis. Even on a local basis, appropriate pollution controls should be able to adequately control emissions of PM, transition metals, and fine PM precursors (such as SO_x).

Little is known about the behavior of Orimulsion in a freshwater spill, and subsequently little is known about how to respond to such a spill. The responsibility for addressing this issue should rest primarily with Bitor and/or the utility using Orimulsion, although EPA should stay abreast of such studies. This should not be construed to imply that EPA should not conduct research as appropriate to ensure that they are able to meet their responsibilities to respond to spills. A study by the National Academy of Sciences on information needs associated with Orimulsion effects, behavior, and response is being funded by EPA and the Coast Guard, and EPA is conducting research to determine characteristics of Orimulsion and to better model its behavior in spills.

A review of an ecological risk assessment of a potential spill in the Tampa Bay, Florida marine environment agreed with the assessment's conclusion that a spill of Orimulsion 100 likely poses a similar or lower risk to Tampa Bay biota than does an equivalent spill volume of No. 6 fuel oil. Although the reviewers of the assessment felt a number of improvements could be made to the assessment, they concluded that none of the improvements would be likely to change the assessment's conclusions. However, the review was limited to the scope of the original assessment, and did not examine other factors that may have significant adverse ecological and health impacts. Nevertheless, as of the writing of this document, there has not been an equally comprehensive assessment of a possible spill of Orimulsion 400 into either marine or freshwater environments.

Further Conclusions
Orimulsion Properties
- Orimulsion is physically and chemically an emulsified hydrocarbon fuel oil with high sulfur, vanadium, and nickel content.

Air Pollutant Emissions
- In comparison to other fossil fuels, Orimulsion will in general emit more pollutants than natural gas, about the same as heavy fuel oil, and less than pulverized coal. These comparisons do not hold for all cases, and are based on emission levels without air pollution control systems.
- Orimulsion contains higher levels of Ni, S, and V than most other fuels, including coal, resulting in higher uncontrolled emissions of SO_2, SO_3, Ni, and V compared to other fossil fuels.
- Uncontrolled PM emissions from Orimulsion are significantly lower than those from pulverized coal, similar to those from heavy fuel oils, and significantly higher than those from natural gas.
- Particles from Orimulsion combustion are generally smaller than those from heavy fuel oil, and significantly smaller than those from pulverized coal combustion.
- NO_x emissions from the combustion of Orimulsion are approximately the same as those from heavy fuel oil, lower than those from pulverized coal combustion, and higher than those from natural gas combustion. NO_x emissions from Orimulsion, like those from other fossil fuels, are sensitive to combustion conditions and design of the combustion system.
- Emissions of organic compounds from the combustion of Orimulsion are very low, similar to those from the combustion of pulverized coal, heavy fuel oil, and natural gas.

Air Pollution Control Technologies
- Commercially available control technologies that are appropriately designed and operated are capable of controlling air pollutant emissions from the combustion of Orimulsion.
- Previous experience with Orimulsion indicates that conversion to the fuel may require significant changes to existing equipment, including air pollution control systems, fuel supply and handing systems, and boiler internal components.

Solid Waste Disposal
- Recovery of Ni and V from Orimulsion ash is currently being conducted. Although untreated Orimulsion ash is less dense than ash from coal or heavy fuel oil, ash handling can be improved through modification of ash hoppers and the addition of water to improve ash agglomeration.

Toxicity
- In general, both formulations of Orimulsion generated PM emissions that were capable of producing significant adverse acute pulmonary toxicity, very similar to the No. 6 fuel oil tested. In all cases, PM from both Orimulsion formulations and the No. 6 fuel oil showed measures of toxicity greater than or equal to either Arizona road dust or saline solution.
- Acute pulmonary toxicity as measured using 5 toxicity markers found the relative toxicity ranking of PM from Orimulsion to be less than or equal to PM from No. 6 fuel oil, except for pulmonary injury as indicated by lactate dehydrogenase (LDH), where Orimulsion 400 showed higher indications of toxicity at lower doses (0.125 and 0.25 mg/ml).

Spills
- Orimulsion is likely to behave much differently in a spill than most other fossil fuels, leading to significant difficulties in cleanup and recovery of spilled fuel, particularly in fresh water. The presence of the surfactant and the density of the fuel are likely to result in spills that do not float and that are not easily contained.

Ecological Risk
- A review by an EPA-chosen expert panel of a utility-funded ecological risk assessment of a potential spill in the Tampa Bay, Florida marine environment agreed with the assessment's conclusion that a spill of Orimulsion 100 likely poses a similar or lower risk to Tampa Bay biota

than does an equivalent spill volume of No. 6 fuel oil. However, the review was limited to the scope of the original assessment, and did not examine other factors that may have significant adverse ecological and health impacts. The reviewers' conclusion may differ for different conditions associated with other combinations of variables such as location, weather conditions, level of fuel use, and diversity and number of biota in the locality. Although the reviewers of the assessment felt a number of improvements could be made to the assessment, they concluded that none of the improvements would be likely to change the assessment's conclusions. While additional factors could also have been included in the assessment, as of the writing of this document, there has not been an equally comprehensive assessment of a possible spill of Orimulsion 400 into either marine or freshwater environments.

Potential for Orimulsion Use
- The most likely use of Orimulsion in the U.S. is as a replacement for heavy fuel oil, due to similarity in handling and combustion properties, the price differential between the two fuels, and the readiness of plants using heavy fuel oil to accept tanker shipments of Orimulsion. These factors would indicate that Orimulsion is most likely to be used along the Atlantic and Gulf coasts in the U.S.
- Orimulsion is designed to be a base load fuel, due to its pricing structure. Utilities may find Orimulsion most attractive as a fuel for increasing utilization of older plants as electricity demands increase.
- As fuel oil prices increase, Orimulsion may become a more attractive alternative fuel.

Data Reported in the Literature
- The full-scale air emissions and pollution control data reported in the literature are consistent with expected results, based on the properties of the fuel, and with EPA's pilot test results. Although these studies have been largely supported by Bitor and/or other interested parties, there is no indication that the data from these studies are any less valid than the results of the pilot-scale study conducted by EPA for this report.

Recommendations
The following recommendations are made with regard to Orimulsion behavior and its potential environmental impacts, and EPA's role in further studies:

1. Based on the these results of Phase I of the Orimulsion Technology Assessment Plan, it is not necessary for EPA to proceed with Phases II and III.

2. From the perspective of air pollutant formation and control, Orimulsion should be considered to be a heavy fuel oil, albeit with some properties that require special attention.

3. Studies of Orimulsion behavior in freshwater spills are needed in the event that Orimulsion is transported along fresh waterways or used in situations where spills can reach fresh water, even indirectly. This research should evaluate the effects and behavior of Orimulsion under different conditions (water density, presence of silt or other solids, energy level of waves) and should evaluate means of containing and responding to spills. Bitor or the end user should be responsible for the cost of any such work that directly supports efforts to market Orimulsion in the U.S. EPA should continue to follow any work conducted by others on the behavior and fate of Orimulsion spills, and should conduct the research necessary to support their legislated responsibility for spill response, outside the scope of the Congressional directive to provide improved scientific information on the environmental impacts of Orimulsion use.

4. Research recommended in a review by an EPA-chosen panel for improvements to a utility-funded ecological risk assessment of a potential spill in the Tampa Bay, Florida marine environment is considered to be the responsibility of Bitor.

Chapter 12
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Appendix A
Conversion of English System to SI System Units

bbl (U.S., petroleum) x 158.987 = L

Btu/hr x 2.93x10^{-4} = kW

(°F - 32) x 0.556 = °C

ft^3 x 0.028316 = m^3

ft^3/min x 0.028316 = m^3/min

gallon x 3.7853 = L

gpm x 3.7853 = L/min

in. x 2.54 = cm

lb/10^6 Btu x 0.43021= g/MJ

lb/10^{12} Btu x 0.43021 = µg/MJ

ppm of NO x 1.230 = mg/Nm^3

ppm of SO$_2$ x 2.620 = mg/Nm^3

ppm of CO x 1.145 = mg/Nm^3

tons x 0.9072 = tonnes

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completing)

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4. TITLE AND SUBTITLE Environmental Impacts of the Use of Orimulsion (R): Report to Congress on Phase 1 of the Orimulsion Technology Assessment Program, Volume 2		**5. REPORT DATE** July 2001
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16. ABSTRACT The report gives results of an evaluation of Orimulsion, a bitumen-in-water emulsion produced in Venezuela, to provide a better understanding of the potential environmental impacts associated with its use as a fuel. Pilot-scale tests were conducted at EPA's Environmental Research Center in Research Triangle Park in North Carolina, to provide data on emissions of air pollutants from the combustion of Orimulsion 100 (the original formulation), Orimulsion 400 (a new formulation introduced in 1998), and No. 6 (residual) fuel oil, commonly used in the U. S. These results, and those of full-scale tests reported in the technical literature, were evaluated to determine the potential air pollutant emissions and the ability of commercially available pollution control technologies to adequately reduce those emissions. Results indicate that carbon monoxide, nitrogen oxide, and particulate matter (PM) emissions are likely to be nearly the same as those from No. 6 fuel oil, that sulfur dioxide emissions can increase if the Orimulsion sulfur content is higher than the fuel it replaces, that the PM generated by Orimulsion 100 and 400 is likely to be smaller in diameter than that generated by No. 6 fuel oil, and that hazardous air pollutants are also likely to be similar to those from No. 6 fuel oil. Conventional control technologies can effectively reduce emissions to very low levels.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group
Pollution	Emission	Pollution Control	13B 14G
Bitumens	Carbon Monoxide	Stationary Sources	11G 07B
Emulsions	Nitrogen Oxides	Orimulsion	07D
Fuels	Particles	Particulate	21D
Combustion	Toxicity		21B 06T
Residual Oils			

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